THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1925.

LXXXII. *Radiation given out by Gases through which Electric Discharges are passing.* *By* Sir J. J. THOMSON, *O.M.*[*]

IN a paper on the electric discharge through gases at low pressures (Phil. Mag. July 1924) I gave reasons for thinking that the ionization in the "negative glow" is due to radiation excited by the cathode rays in the gas through which they pass.

The following paper contains an account of a series of experiments made with the object of obtaining direct evidence of the existence of this radiation and of throwing some light on its properties and origin. This radiation is not penetrating enough to pass through the glass of the discharge-tube, so that to study it we must use some method by which it can be detected inside the tube or, at any rate, before it has had to pass through an appreciable thickness of solid matter.

The most sensitive methods for detecting such radiations depend on the electrical effects, such as those of ionization or of photo-electricity, which they produce. As the electrical discharge fills the tube with ions which would disturb any electrical detector of the radiation if they came into contact with it, it is necessary to screen off the ions from the detector.

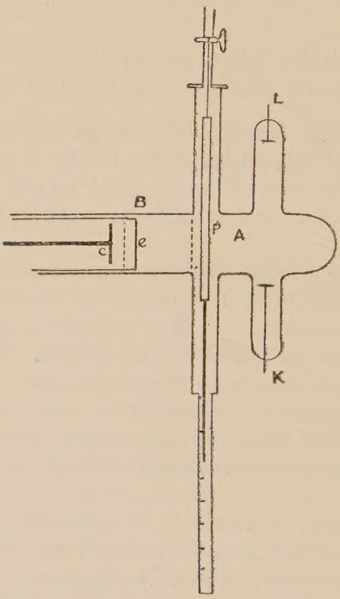
I have used three kinds of screens: the first of these is a material screen of very thin celluloid; in the second there is no solid matter between the detector and the gas in the tube,

[*] Communicated by the Author.

but the ions are screened off by a strong electrostatic field; in the third type of screen the electrostatic field is replaced by a magnetic one.

I shall commence with the experiments made with the first type of screen. My assistant, Mr. Everett, has found a very convenient way of making screens of this kind : a drop of a very weak solution of celluloid in ether is put on the top of a pool of mercury and allowed to evaporate, leaving a thin circular disk of celluloid floating on the mercury, from which it can easily be detached. From very weak solutions it is easy to get celluloid disks thin enough to show brilliant colours of thin plates and whose mass per unit area is less than that of a layer 1/10 of a millimetre thick of air at atmospheric pressure. These films are very tough although they are so thin, and one about a centimetre in diameter can sustain without rupture a difference of pressure on its two sides of several millimetres of mercury.

Fig. 1.



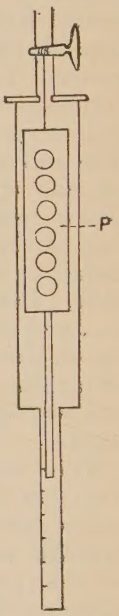
The arrangement used to detect the radiation with a screen of this kind is shown in fig. 1. K is the cathode and L the anode of a discharge-tube. When the discharge passes, the cathode rays pass through the gas in front of K and produce the dark space and the negative glow.

A horizontal side tube B is fused on to the tube A at a place in front of the cathode so that the radiation from the negative glow passes down this tube; the portion of the tube A opposite B is blown out so as to prevent the impact of cathode rays on the glass opposite B. The detector of the radiation is placed in a tube which fits into B. This detector consists of a metal disk *c* carried by a metal rod, which is carefully insulated and connected with one pair of quadrants of a Dolezalek electrometer. The sensitiveness of the electrometer was such that it gave a deflexion of 300 scale divisions per volt. As very wide ranges of current had to be measured a battery of condensers, giving a capacity which could be varied from ·001 to 1 microfarad, was arranged so that any capacity within these limits could be added to the electrometer. The capacity of the electrometer system and its connexions with the disk was ·00014 mf. The rod and disk are surrounded by a metal tube connected with the earth. The end of this tube nearest to the discharge-tube is closed by one of the thin celluloid films *e* just described; wire gauze connected with the earth is placed in front of and behind the film so as to shield the disk *c* from electrostatic induction arising from charges of electricity in the discharge-tube. The other end of the tube carrying the celluloid disk *e* is closed and a wire from *c* to the Dolezalek passes through an ebonite plug in this end of the tube. The disk *c* in most of my experiments was about 2 mm. from the celluloid film and was very nearly of the same diameter (1 cm.) as the film itself.

This arrangement in which a screen of celluloid is used has many advantages; thus, as there is no communication between the tube enclosing the disk and the tube through which the electrical discharge passes, the pressure of the gas round the disk *c* can be altered without affecting the pressure of the gas in the discharge-tube; this is an important point, for valuable evidence as to the effects produced by the radiation can be obtained by altering the pressure of the gas round *c*. The disadvantage of this method is that before the radiation can be investigated it has to pass through a film of celluloid. We shall see later on that of the radiation coming from the negative glow only a fraction of one per cent. gets through a film of celluloid so thin that it shows brilliant colours of thin plates and thus could not have been much more than 3×10^{-5} cm. thick. This arrangement is thus not suitable for studying the most absorbable type of radiation, though it is the most convenient for studying radiation "hard" enough to penetrate the film in appreciable amounts. I shall, before proceeding to discuss the more absorbable radiations, describe some of the results which have been obtained with this type of detector.

To measure the absorption of the radiation by different substances so as get some idea of its wave-length, the following arrangement was used. A plate of lead pierced with six circular holes, the size of the celluloid window, could be moved vertically up and down by a cord passing over a winch, as shown in fig. 2. This plate passed quite close to the celluloid window, between it and the negative glow. Of the six holes in the plate one was left open, another was closed by a celluloid film of the same thickness as that used for the screen, another was covered by aluminium-foil 5×10^{-5} cm. thick, another by two layers of this foil, the fifth by gold-leaf 7×10^{-6} cm. thick, and the last by two layers of this leaf; thus, by comparing the effect produced on the disk *c* when the winch was turned so as to bring the free opening in the plate in front of the window with that when it was turned so as to bring either the aluminium, gold-leaf, or celluloid into this position, the absorption by these substances could be determined.

Fig. 2.



The electric discharge through the tube was produced by a high potential dynamo made by Evershed and Vignolles, which gave steady potential differences up to 5500 volts; for higher voltages an induction coil was used; experiments were also made using a hot tungsten filament for cathode.

When the electric discharge is passing through the tube and the cathode rays are traversing the gas in front of the window, the electrometer connected with the disk *c* is deflected, showing that the disk is receiving a charge of electricity. Before the discharge starts the quadrants of the electrometer connected with *c* are put to earth, the other pair of quadrants are permanently earthed, then if *c* is disconnected from earth and the discharge started, there is a deflexion of the electrometer, continuously increasing at first, but ultimately attaining a constant value; the amount and even the sign of the deflexion depends upon circumstances, such as the pressure of the gas in the discharge-tube, the potential difference between the electrodes of the tube, to some extent upon the position of the anode, and also upon the pressure of the gas round the disk connected with the electrometer.

The electrical effects which the radiation might be expected to produce are (1) photoelectric effects, (2) effects due to the ionization of the gas between the disk *c* and the earthed wire gauze.

Let us consider the effect on the electrometer produced by the photo-electric effects. In consequence of this effect, the radiation falling on *c* would cause it to emit negative electricity: this would leave *c* and the electrometer with a positive charge; whereas, except when the pressure in the tube containing *c* is very low and the potential difference large, the charge in the electrometer is generally negative. If this negative charge is due to photo-electric effects it must be because the photo-electric effect of the celluloid film is greater than that of the disk, so that the stream of negative electricity coming from the film towards the disk is greater than that going from the disk towards the film. If this were the explanation of the negative electrification of the disk, then if instead of the celluloid screen we used one consisting of a strong electric field, the disk ought always to acquire a positive charge, as there is no other photo-electric source of negative electrons to counterbalance the stream coming from the disk itself; we shall see, however, that with these electrostatic screens the charge in the electrometer is frequently negative. This proves that in some cases the most important factor is not the photo-electric effect, but must arise from the ionization of the gas between the disk *c* and the gauze. This negative charge would result from the negative electrons diffusing more rapidly to the disk than the positive ions; the disk would charge up negatively and accelerate the flow of the positive ions and retard that of the negative until the flow of the one was equal to that of the other.

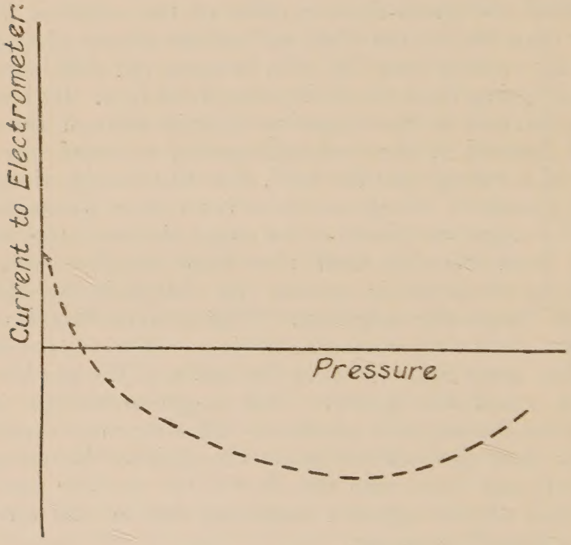
In addition to the effect due to the difference of the rates of diffusion, the experiments give some evidence that, when the gas is ionized by the radiation, more electrons are emitted in the direction in which the radiation is travelling than in the opposite direction, so that a stream of ionizing radiation is accompanied by a stream of electrons in the same direction.

Very direct evidence as to the importance of the ionization effect on the charges received by *c* is obtained when we investigate the effect of altering the pressure of the gas round *c*, while leaving that in the discharge-tube unaltered;

the form of apparatus shown in fig. 1 enables us to do this without difficulty, as there is no communication between the tube through which the electric discharge passes and the one round *c*.

Starting with a very low pressure round *c* and gradually increasing it, we find that the rate at which *c* receives negative electricity increases with the pressure of the gas, and at some stages the rate of increase of the deflexion of the electrometer is more rapid than the rate of increase in the pressure. The rate of increase with the pressure finally falls off as the pressure round *c* gets greater, and there is often a pressure at which the rate of charging up has a maximum value.

Fig. 3.



The range of pressures round *c* used in these experiments was from that of the best vacuum which could be obtained by the use of charcoal cooled by liquid air to about 4 mm. of mercury, which was about the greatest pressure the celluloid film would stand without breaking. When the pressure round *c* was exceedingly low, *c* generally received a positive and not a negative charge. The relation between the rate of charging up of the disk *c* (the ordinate) and the pressure of the gas round *c* (the abscissa) is of the character represented in fig. 3, when the discharge is produced by the continuous high-tension dynamo and the potential difference is from 1000 to 5000 volts.

These results show, I think, that in this case the negative charge is due to the ionization effects; these would vanish in a perfect vacuum, and would increase with the pressure of the gas round *c*.

The photo-electric effects tend to give the electrometer a positive charge, while the effects due to ionization tend to give it a negative one; thus the charge acquired by the electrometer may be positive or negative according as one or other of these effects predominates. Increase of pressure round *c* will increase the ionization effects relatively to the photo-electric ones and thus tend to make the charge given to the electrometer negative. Increase in the "hardness" of the rays in the discharge-tube will favour the photo-electric effect, because the harder rays are not so readily absorbed by the gas between *c* and the gauze and so do not produce so much ionization as the softer ones. This effect can readily be observed by using an induction coil to produce the discharge and gradually diminishing the pressure in the discharge-tube by means of a tube filled with charcoal coolod with liquid air. When the pressure is fairly high (say ·1 mm. of Hg) and the discharge goes easily, as shown by the shortness of the equivalent spark-gap, the electrometer will receive a negative charge, but as the pressure falls and the spark-gap increases the negative charge will diminish, will vanish, and then be replaced by a positive one.

In the preceding experiments the cathode is placed so that the cathode rays do not strike against those parts of the walls of the discharge-tube which have a view of the window through which the radiation passes on its way to the testing apparatus; if the cathode rays are bent by a magnet so as to strike against the parts of the glass walls of the discharge-tube opposite to the window the charges received by the electrometer are very much increased.

Character of the Radiation in the Tube.

The character of that part of the radiation in the tube which is able to penetrate the celluloid window of the testing apparatus can be determined by measuring the ratio of the rate of charging up of the electrometer when screens of various substances are put before the celluloid window to the rate when no such screens were interposed. The results of such measurements are given in the following table. The thickness of the celluloid film was estimated from its optical properties as about $3\ 10^{-5}$ cm. The thickness of the gold screen was such that 100 sq. cm. of the leaf weighed ·014 gr., that of the aluminium such that 100 sq. cm. weighed ·0142 gr. The discharge was produced by the high potential dynamo. In the table, r represents the ratio of the rate of charging up of the electrometer when the underwritten screen was inserted to the rate before insertion.

Gas in the discharge-tube—hydrogen.

Potential difference between the electrodes 1500 volts.

r. Celluloid.	r. Aluminium.	r. Gold.
·4	·3	·125

Potential difference between the electrodes 5000 volts.

·6	·6	·16

Gas—helium.

Potential difference between electrodes 1500 volts.

·5	·38	·12

Potential difference 5000 volts.

·6	·57	·18

Gas—oxygen.

Potential difference 1500 volts.

·47	·38	·125

Potential difference 5000 volts.

·52	·45	·15

If μ is the coefficient of absorption of the rays by aluminium, ρ its density, and t its thickness, since 100 cm.^{2} weighed ·0142 gr.,

$$10^2 \times \rho \times t = {\cdot}0142 \; ; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

while at 1500 volts, taking the mean of the absorptions for aluminium,

$$\epsilon^{-\mu t} = {\cdot}36,$$

so

$$\mu t = {\cdot}95,$$

so that from (1)

$$\frac{\mu}{\rho} = 6{\cdot}7 \times 10^3.$$

For the K radiation of chromium, whose wave-length is $2{\cdot}2 \times 10^{-8}$, μ/ρ is equal to 136. If we assume the usual law connecting the absorption of the radiation with its wave-length λ, *i. e.* that μ varies as λ^3, the wave-length corresponding to $\mu/\rho = 6{\cdot}7 \times 10^3$ is $8{\cdot}1 \times 10^{-8}$ cm.; the voltage corresponding to this radiation is 1500 volts, which is exactly the voltage applied to the discharge-tube. It must be remembered that all the radiation, even when there is no screen before the celluloid window, has to pass through this window before reaching the detector, and that any radiation soft enough to be absorbed by the window would not be detected by this method ; we shall see directly that by far the greater part of the radiation in the tube is so absorbed, so that by this method we are dealing only with the most penetrating radiation.

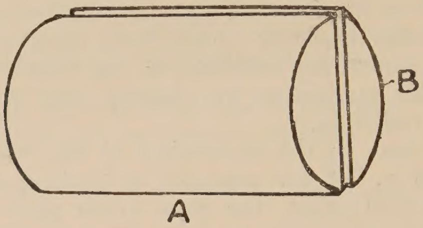
It will be seen by the comparison of the results given in the table on p. 768 for potential differences of 1500 and 5000 respectively that the rays which pass through the celluloid film get on the average more penetrating as the potential difference applied to the discharge-tube increases. The character of this radiation thus depends on the potential difference. I made a large number of experiments to see if it depended on the nature of the gas in the discharge-tube. I measured the coefficients of absorption in aluminium, gold, and celluloid with air, oxygen, hydrogen, and helium in the discharge-tube, and with the same potential difference between the electrodes could not be sure that there was any difference in the radiation produced by the change of gas ; the difference, if any, is certainly small : these observations only refer to the harder radiations which can pass through the celluloid film. The amount of radiation is less in the light gases than in the heavy ones.

The type of radiation in a tube with a given gas at constant pressure may depend upon the means used to send the discharge through the tube ; thus the type of radiation depends to some extent upon whether the discharge is produced by a continuous-current dynamo or by an induction coil, and if by an induction coil, upon the size of the coil and the nature of the interrupter. This might be expected, as the potential difference between the electrodes often depends upon the character of the discharge and is not determined solely by the pressures.

Very "Soft" Radiation in the Tube.

In the previous method all the radiation has to pass through a celluloid film before reaching the detector, so that only the "rays" hard enough to pass through the film come under observation. To study the more absorbable types of radiation I have used screens by which the ions in the discharge-tube are screened off from the detecting apparatus connected with the electrometer, not by material screens, but by screens of intense electric and magnetic forces. One arrangement I used is shown in fig. 4.

Fig. 4.



The halves A and B of a cylindrical brass rod fit tightly into a glass tube fitted into the tube which holds the disk attached to the electrometer. A and B are insulated carefully from each other and are connected respectively with the poles of a battery of small storage-cells so that potential differences up to 1000 volts can be maintained between them. The distance between the plain faces of A and B is 1 mm., and their length 3 cm. A simple calculation will show that when the difference of potential between A and B is 600 volts (the difference most frequently used in these experiments), any ions, whether positive or negative, attempting to pass between A and B would be driven against one side or the other unless their energy were greater than that corresponding to well above 100,000 volts. This was also established directly by experiment, as long before the difference of potential between A and B reached 600 volts an increase in the potential difference produced no effect on the deflexion of the electrometer. The fact that over very wide ranges of potential difference the deflexion is independent of the potential shows that no appreciable radiation is produced by driving the ions against the sides of the slit.

When this arrangement was put in place of the celluloid screen ions would be stopped, but the radiations would reach the detector without passing through any matter other than the gas in the tube; this is a great advantage. The disadvantages are, firstly, since A and B have to be close together to get a strong electric field, the area of the window through which the radiation from the discharge passes is much less than when the celluloid film is used; and secondly, since there is direct communication between the discharge-tube and the one surrounding the detecting apparatus the pressures in these two tubes are always the same, whereas when the film is used either of these pressures can be varied independently of the other.

I have also used a strong magnetic field instead of an electric one to screen off the ions, but found the electric one the more convenient.

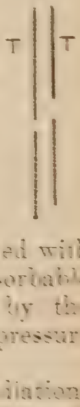
Absorption of Rays by the Celluloid Film used in the previous experiments.

We can measure by the electrostatic screen how much of the radiation was stopped by the celluloid. As one of the openings in the sliding plate (fig. 2) can be stopped by a film of the same thickness as that used for the window in the first experiments, all we have to do is to measure the rate of charging up of the electrometer, (1) when a free opening in the moving plate is opposite the slit of the electric screen, and (2) when an opening filled by the celluloid film is in the same position. The results are very remarkable: with oxygen in the discharge-tube and a potential difference of 3000 volts between the electrodes, the rate of charging of the electrometer when the radiation did not pass through the celluloid was more than 100 times greater than when the rays passed through it. So that in the previous experiments we have only been dealing with a small percentage of the radiation in the tube; the great bulk of this radiation when the potential is comparable with 3000 volts is completely stopped by a layer of celluloid about $3 . 10^{-5}$ cm. thick. By moving the lead plate carrying the various diaphragms up and down we can insert screens of celluloid, aluminium, and gold in the path of the radiation and find the absorption produced by them. The relative amounts of the soft radiation stopped by these screens differ from those for the harder radiation which in the earlier experiments had been filtered through a celluloid screen. Thus with the harder radiation the gold always transmitted far less than either the aluminium or the celluloid (see p. 768), while with the softer radiation passing through the electrostatic screen the gold transmits twice as much as the aluminium or celluloid. I noticed, many years ago, in some experiments I made on very soft Röntgen rays generated by low-speed electrons from a hot cathode, that relatively to aluminium gold absorbed much fewer of the softer than of the harder rays. This, I think, is due to much of the radiation having wave-lengths comparable with the characteristic radiations of aluminium and carbon, so that the absorption of these substances is abnormal.

The conflict between the photo-electric effect and the ionization one is shown quite as distinctly with the electric screen as with the celluloid one. For when the pressure is fairly high we find that with the electric filter the electrometer receives a negative charge, but as the pressure is diminished the negative charge changes to a positive one. At the higher pressures the ionization has the upper hand, and this produces a flow of electrons to the electrometer, the photo-electric effect produces a flow of electrons from the disk, and this tends to make the charge in the electrometer positive: this effect does not diminish as the pressure diminishes, while that due to the ionization does, so that at very low pressures the electrometer must acquire a positive charge.

To make sure that the charge acquired by the electrometer arose from the effect of radiation and was not due to the passage of gas in some abnormal state between the jaws of the electric screen, I tried the following experiment. I placed in front of the jaws of the electric screen the screen represented in fig. 5 made of two sheets, T and T′, of thick tinfoil with holes bored through them as in the figure. This screen was opaque to radiation travelling in the direction necessary to get through the electric screen, but was pervious to a flow of gas from one side to the other. This screen stopped completely any charging up, positively or negatively, of the electrometer. Hence we conclude that this charging is due to radiation coming from the discharge-tube.

Fig. 5.



The preceding experiments show that a tube through which an electric discharge is passing is filled with radiation, some of which is of an exceedingly absorbable type, so absorbable that it is practically stopped by the equivalent in mass of a layer of air at atmospheric pressure a few millimetres thick.

The proportion which these very absorbable radiations bear to the other radiations in the discharge-tube depends upon a great variety of circumstances, on whether for example the discharge is produced by an induction coil or by a steadily-maintained potential difference. The amount of radiation in the discharge-tube has covered a very wide range in these experiments. Taking as the unit the deflexion per second of the electrometer when connected up with a condenser whose capacity is ·1 microfarad, the output of radiation has varied from ·001 to 4·5. The results of these experiments show that when the output is large there is a much larger proportion of the more absorbable rays than when it is small.

The fraction of the radiation passing through one layer of gold leaf when oxygen was in the tube has varied from 1/36 to 1/1000. The larger value occurred with a steady difference of potential equal to 4000 volts, the pressure was ·015 mm. of Hg and the output of radiation ·015. The smallest value was when the discharge was produced by an induction coil: the output of radiation was 3·4, the equivalent spark-gap 5 mm., and the pressure ·003 mm.

In hydrogen the range of absorption produced by the gold-leaf was from 1/80 to 1/400, the largest value was obtained with a hot lime cathode under a constant potential difference of 3000 volts at the pressure ·045 mm., and an output of ·08, the smallest value with an induction coil, spark-gap 4 mm., output 2·2, and pressure ·042 mm.

In helium the fraction getting through the gold-leaf varied from 1/40 to 1/300, the largest occurred with the discharge from a coil with an output ·35, pressure ·084 mm., the smallest when the coil had an output of 3, pressure ·062. Films of silver and aluminium showed similar effects, though their absorption was greater than that of the gold-leaf.

Absorption of radiation by gas.

The negative glow may be well developed when the pressure in the discharge-tube is as low as ·01 mm. of mercury. If, as we have supposed, the ionization in the negative glow is produced by the soft radiation, then this radiation must suffer appreciable absorption when passing through a layer of gas at this pressure comparable in thickness with the linear dimensions of the negative glow, say 10 cm. The mass of a layer of gas 10 cm. thick at the pressure ·01 mm. of mercury is equivalent to that of a layer of air 1/760 mm. thick at atmospheric pressure, this has about the same mass as a celluloid film 10^{-7} cm. thick. Films as thin as this are not manageable, so we cannot by means of them detect whether there is any radiation in the discharge-tube as soft as that indicated.

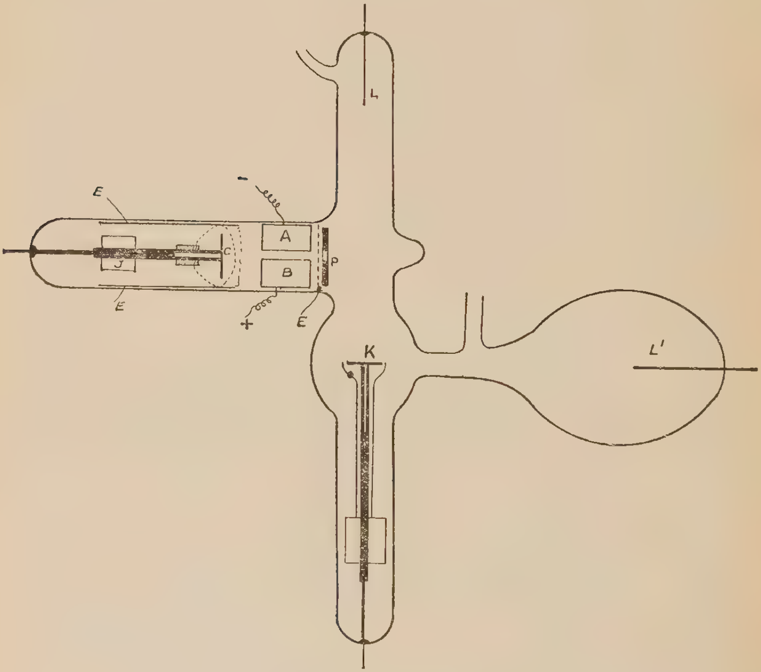
Absorption of radiation by air.

We can, however, by the following method test the absorption produced by the passage of the radiation through different lengths of the gas actually in the discharge-tube.

The arrangement is that represented in fig. 6.

The disk *c* and the wire gauze in front of it are rigidly connected with a metal tube which can slide along the metal rod connecting the disk *c* with the electrometer. A piece of iron J is attached to the tube and this can be made to move backwards and forwards along the tube by a magnet. The wire gauze in front of the disk is insulated from it and is kept connected with earth by a thin wire spring. By altering the distance of the disk from the end of the electric screen we can alter the length of path traversed by the rays before they reach the disk, and by making measurements when the disk is in different positions we can determine the absorption of the rays when they pass through a known length of gas at the pressure in the discharge-tube. For these experiments the opening in the electric screen was stopped down until the aperture was so small that all the rays passing through it fell upon the disk even when it was moved to the most distant position at which measurements were made.

Fig. 6.



Experiments with this apparatus gave very interesting results, these varied with the nature of the gas and the pressure in the tube, but observations made with oxygen at the pressure ·01 mm. bring out many of the points of interest.

When the disk is close up to the electric screen the electrometer receives a *negative* charge, indicating the predominance of the ionization effect ; as the disk is moved further away from the screen the rate at which the electrometer receives a negative charge diminishes, until when the distance between the disk and the screen is about 15 mm. the electrometer does not charge up either positively or negatively. After passing this point the electrometer acquires a *positive* charge, indicating that now the photo-electric effect is predominant ; the positive effect increases up to a maximum when the distance of the disk from the end of the electric screen is about 30 mm., after this it begins to diminish and goes on diminishing continuously as the distance between the disk and the screen is increased to its limiting value, 50 mm. Thus, as the length of path of the radiation through the gas increases the character of the radiation changes, just as the colour of non-homogeneous light changes when it passes through a medium which absorbs one colour more than another.

With the radiation we are considering, which includes a continuous spectrum, the radiation of longer wave-length, which is the more efficacious in providing ionization, is the more easily absorbed, and thus absorption would make the negative effects due to ionization diminish more rapidly as the length of path of the radiation through the gas increases than the positive effects due to photo-electricity, so that at a certain distance the latter may begin to predominate. As radiation of all kinds is absorbed to some extent, there will be a distance at which the positive effect is a maximum. This explanation is confirmed by the results which are obtained when the pressure is altered ; thus when the pressure is considerably lower than that in the last experiment the positive effect is the only one observed, even when the disk is put quite close up to the electric screen ; it reaches a maximum at a distance from the screen depending upon the pressure and then diminishes. At these low pressures the ionization effect is relatively less important than the photo-electric one and so is not able to overpower it. On the other hand, at pressures considerably higher than ·01 mm. the negative effect is the only one observed, and this diminishes continuously as the distance between the disk and the screen is increased. These experiments show I think conclusively that even at the low pressures occurring in the discharge-tube there is an appreciable amount of absorption of the radiation and therefore the production of an appreciable amount of ionization in the space of a few centimetres of gas.

Similar experiments were made with hydrogen and helium, and it was found that the pressures at which the change from the negative to the positive effect occured was far higher in hydrogen than in oxygen, and again far higher in helium than in hydrogen. This is what we should expect as the negative effects are due to the absorption of the rays, and this absorption at equal pressures is much greater in oxygen than in either hydrogen or helium.

Amount of absorption by the gas in the discharge-tube.

The radiation in this tube is very complex, it is probable that it is in the main a continuous X-ray spectrum up to a frequency ν where $h\nu = Ve$; here V is the potential difference between the electrodes in the tube and h Planck's constant. Superposed on this there will be those characteristic radiations of the gases in the tube which have a frequency less than ν. The absorption of the different parts of the spectrum will vary rapidly with the wave-length of the radiation, and as we do not know the distribution of energy among the various wave-lengths, we cannot do more than form an estimate of an average value of the absorption.

In the case we have just been considering an increase of 1·5 cm. in the distance through which the radiation travels changes the sign of the effect, and after a further increase of 1·5 cm. the positive effect is a maximum, while another 2 cm. reduces the positive effect to about two-thirds of its maximum. This shows, I think, that the intensity of a considerable part of the radiation must be reduced to $1/\epsilon$ of its value in a length comparable with about 3 cm. This corresponds to a coefficient of absorption in oxygen equal to 1/3 at ·01 mm. pressure. This is equivalent to an absorption coefficient of $2{\cdot}53 \times 10^4$ at atmospheric pressure. The absorption coefficient at this pressure in air for the K radiation of iron, whose wave-length is 1·93 Å, is 2×10^{-2}, hence, assuming that the absorption is proportional to the cube of the wave-length, the wave-length of the very absorbable radiation we are considering would be about 200 Å, the energy corresponding to this radiation is about 60 volts.

The intense absorption of the radiation by gases has an important application to the theory of the structure of light. It shows I think that the region in which the energy of this very absorbable radiation is concentrated, the quantum, must be considerably greater than the region occupied by an atom. For the radiation to be absorbed the quantum must pass over an electron, and when the absorption occurs in a few millimetres of the gas at the pressure of ·01 mm. of mercury, the quantum must have a cross-section considerably greater in area than that of a circle whose radius is 10^{-8} cm., if it is to meet with one electron while passing over the distance within which it is absorbed. Thus the quantum would have to be of atomic dimensions, even if every collision with an electron resulted in absorption, an exceedingly improbable assumption. From what we know of the absorption of radiation, particularly its variation with the wave-length, it is much more probable that the quantum has to make on the average a considerable number of collisions with electrons before absorption takes place, this would require the cross-sections of the quantum of these very absorbable radiations to be considerably greater than the cross-section of atoms. I gave in the 'Philosophical Magazine,' Sept. 1924, a theory of the structure of light in which the quantum is regarded as a ring made up of lines of electric force, the circumference of which is equal to the wave-length of the light. For the characteristic radiation from the heavier elements the wave-length is considerably smaller than atomic dimensions, but for the soft radiations we are considering the wave-length is several times greater than the atomic radius.

Radiations from different parts of the discharge.

The luminosity of the discharge in the neighbourhood of the cathode varies enormously at different distances from the cathode, thus we have at the surface of the cathode a thin layer of velvety glow, this is succeeded by the dark space which emits very little visible light, following this we have the bright luminosity of the negative glow; the transition from the dark space to the negative glow is often, as in oxygen, exceedingly abrupt, and the position of the boundary can be determined to the fraction of a millimetre. It is important from the point of view of the theory of the discharge to ascertain if this large variation in luminosity is accompanied by a corresponding variation in the emission of the ionizing radiation. To test this I arranged that the cathode K, fig. 6, could by means of a magnet be moved backwards and forwards along the tube; when the cathode was as far back as possible, the negative glow was opposite the slit through which the radiation passed to the testing apparatus; as it was moved forward various parts of the negative glow came at first in front of the slit, then the negative glow passed beyond the slit and was succeeded by the dark space, various parts of the dark space then passed in front of the slit until finally the cathode itself went past the slit.

The following example shows the kind of variation that is found in the radiation coming from different regions near the cathode, the length of the dark space in this experiment was 30 mm. :—

	Distance of slit in front of cathode.	Radiation.	Fraction passing through gold-leaf.
Dark space	0	10	1/150
	10 mm.	25	1/120
	20 mm.	23	1/125
	30 mm.	18	1/108
Glow	40 mm.	15	1/216

Thus, there is a falling off in the intensity of the radiation close to the cathode, but otherwise there is a steady increase in the radiation as we proceed from the negative glow into the dark space, the gas in the discharge-tube was oxygen at the pressure of ·014 mm. There was bright luminosity in the negative glow and a sharply-defined boundary between the negative glow and the dark space, so that there was discontinuity in the brightness of the luminosity. It will be seen from the figures that there was no indication of any abrupt variation in the emission of the absorbable ionizing radiation. In addition to the amount of the radiation coming from the different parts of the discharge I measured also the absorption of this radiation by gold-leaf at different places, the results are given in the third column, it will be seen that the rays from the part of the negative glow furthest from the cathode are the most easily absorbed, and that inside the dark space there is not much variation until we get quite close to the cathode when the rays become of a softer type.

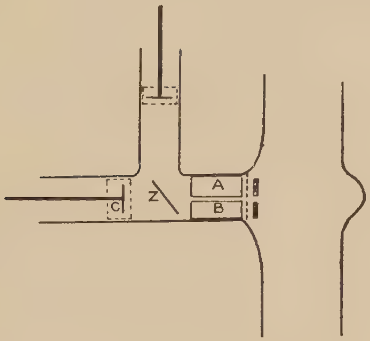
Similar results were found when the gas in the discharge-tube was hydrogen or helium, though in those gases the changes in the luminosity are not so abrupt as in oxygen.

When the direction of the discharge was reversed, so that the electrode K, fig. 6, was anode, and L or L′ cathode, ionizing radiation could be detected coming from the region near the anode ; it was, however, small compared with that coming from near the cathode, although when an induction coil was used the current passing through the tube was much larger when L′ was cathode than when it was anode.

Reflexion of the Rays.

Experiments were made to see if any reflexion could be obtained from polished metallic surfaces. For this purpose the following arrangement was used. Z is a brightly polished disk of zinc, supported by a rod placed in a horizontal tube which joins the main tube B just behind the two pieces of brass A, B which form the electrical filter ; a vertical tube provided with an insulated disk connected with the electrometer and provided with arrangements for measuring the electrical effect, is fused to the tube so as to be above Z and in such a position that rays reflected from Z would strike the disk in this tube. The rod supporting the disk Z could by the action of a magnet on a piece of iron attached to it be pushed forward, so as to be in the path of the radiation coming from the discharge, or drawn back in the tube so as to allow the radiation to strike against the disk *c*. The rod could also be turned round by a magnet and the disk rotated through a considerable angle. Measurements were made first with Z drawn back in the tube and the disk *c* connected with the electrometer, we shall call the deflexion of the electrometer the direct effect. The disk Z was now pushed forward and the electrometer connected with the disk in the vertical tube. Z was now rotated and it was found that when it was in a certain position there was an appreciable deflexion of the electrometer ; that this is due to a true reflexion of the rays is shown by the fact that the deflexion of the electrometer ceases when Z is rotated through a small angle in either direction from the position in which the deflexion is a maximum. The reflector Z was connected to a positive potential of 600 to prevent the emission of electrons.

Fig. 7.



The ratio of the reflected to the direct effect varied with the potential difference between the electrodes of the discharge-tube; it was greater when the potential difference was large than when it was small, the maximum I observed when oxygen was in the discharge-tube was 7 per cent. With hydrogen in the tube the value of this ratio was smaller, never in my experiments exceeding 5 per cent.; while in helium it was much smaller, the maximum value being one-half of one per cent.

The other side of the zinc disk was covered with a smooth layer of paraffin wax. There was a slight deflexion of the electrometer when the disk was rotated through 180° so as to replace the polished zinc reflector by a paraffin one, the effect was, however, small—generally about 1/7—of that produced by the polished surface.

These experiments show that when cathode rays pass through a gas Röntgen rays are generated. These rays are not all of one kind, some of them have wave-lengths very much shorter than those corresponding to the characteristic radiation of the gas, the indications are that they form a continuous spectrum, the limiting frequency ν being given by Planck's relation, $h\nu = \mathrm{E}$ where E is the energy of the cathode ray. Very little seems to have been done on the generation of the continuous Röntgen ray spectrum by the passage of electrons through gases. We may as a guide to what may be expected try to connect the absorption of Röntgen rays by a gas on which a great many experiments have been made with the emission of the rays by the impact of electrons. Let us suppose that we have an enclosure at a temperature high enough to include Röntgen rays among the radiation; the energy of rays having a frequency between ν and $\nu + d\nu$ is by Planck's law, when $\epsilon^{-h\nu/\mathrm{R}\theta}$ is small, proportional to

$$\epsilon^{-\frac{h\nu}{\mathrm{R}\theta}} \nu^3 d\nu,$$

and the number of quanta per unit volume having energy between these limits is therefore proportional to

$$\frac{1}{h} \epsilon^{-\frac{h\nu}{\mathrm{R}\theta}} \nu^2 d\nu.$$

Now suppose that there are molecules of a gas in this enclosure, these will absorb the radiation and to keep things in a steady state must give out on the average as much radiation as they absorb. The number of quanta striking a molecule of the gas in unit time will be proportional to

$$\epsilon^{-\frac{h\nu}{R\theta}}\,.\,\nu^2 c\,.\,d\nu,$$

where c is the velocity of light. Assuming that the absorption is proportional to the cube of the wave-length, *i.e.* to $1/\nu^3$, the chance of one quantum being absorbed on collision varies as $1/\nu^3$; hence the number of quanta of Röntgen radiation absorbed by the molecule per second is proportional to

$$\epsilon^{-\frac{h\nu}{R\theta}}\,.\,c\,.\,\frac{d\nu}{\nu}.$$

Now let us consider the emission, which we shall suppose is due to the impact of electrons. The number of electrons having velocities between v and $v+dv$ is proportional to

$$\epsilon^{-\frac{mv^2}{2R\theta}}\,.\,v^2 dv.$$

The number of these which collide with the molecule in unit time is proportional to

$$\epsilon^{-\frac{mv^2}{2R\theta}}\,v^3 dv.$$

Let us suppose that the chance of their producing a Röntgen ray of frequency between ν and $\nu+d\nu$ is

$$f\left(\frac{mv^2}{2},\,\nu\right)d\nu.$$

Then the emission of the rays will be proportional to

$$d\nu\int_{v_1}^{\infty}\epsilon^{-\frac{mv^2}{2R\theta}}\,v^3 f\left(\frac{mv^2}{2}.\,\nu\right)dv.$$

Where the lower limit of v is given by the equation

$$\tfrac{1}{2}mv_1{}^2 = h\nu,$$

this integral since the emission is equal to the absorption must be equal to

$$\epsilon^{-\frac{h\nu}{R\theta}}\,c\,\frac{d\nu}{\nu}.$$

A solution of this integral equation is

$$f\left(\frac{mv^2}{2},\,\nu\right)=\frac{C}{\frac{mv^2}{2}\,\nu}.$$

So that the chance of an electron producing a quantum of radiation whose frequency is between ν and $\nu+d\nu$ is proportional to $\frac{1}{\mathrm{T}}\frac{d\nu}{\nu}$, where T is the kinetic energy of the electron. Since the energy in the quantum is $h\nu$, the energy emitted will be proportional to

$$\frac{d\nu}{\mathrm{T}}.$$

The value of ν will depend on the circumstances of the collision, such as the smallest distance between the electron and the centre of the atom, or of some of the electrons in the atom. The maximum value of ν will be equal to T/h; we shall give reasons for thinking that there may be a minimum whose frequency is equal to that which just produces ionization in the gas. When we have a great many electrons all having approximately the same energy, the energy in the radiation having frequencies between n_1 and n_2 emitted per second by a given number of molecules is proportional to

$$\frac{n_1-n_2}{\mathrm{T}}.$$

The total quantity of energy radiated is obtained by putting $n_1=\mathrm{T}/h$, and $n_2=\mathrm{T}_0/h$ where T_0 is the energy required to ionize the gas; using these values in the preceding expression we find that the average energy generated by a single collision of electrons, all having the same amount, T, of kinetic energy is proportional to

$$1-\frac{\mathrm{T}_0}{\mathrm{T}}$$

and thus as soon as T gets large compared with T_0, is nearly independent of the kinetic energy. The electrons with large amounts of energy give radiations over a larger range of frequencies than those with smaller amounts, but the density of the energy is not so great. Though at each collision the fast electron may not produce much more radiant energy than the slow one, yet it can make many collisions before its energy gets so much reduced that it is unable to generate Röntgen radiation, so that the total amount of radiant energy produced by the fast one will be much greater than that produced by the slow.

On the average, the energy contributed to the continuous spectrum for one collision will be independent of the energy of the electron. The number of collisions an electron makes before losing its energy is proportional to the square of the energy (J. J. Thomson, 'Discharge of Electricity through Gases,' 2nd Edition, p. 378), hence the energy in the Röntgen radiation produced by a given number of electrons will be proportional to the square of the energy of the electrons, a result which has been confirmed by a large number of investigators.

Hitherto we have not considered what determines the wave-length of the radiation produced when an electron with a given amount of energy strikes against an atom. In the case of the emission of the characteristic radiation from an atom, the radiation seems to occur when an electron loses potential energy by falling from a place where this is great to one where it is smaller, the potential energy lost instead of being converted into an increase in the kinetic energy of the electron is converted into radiant energy, and the frequency of the radiation, ν, is given by

$$h\nu = \text{loss of potential energy.}$$

Now when an electron passes through an atom and comes into collision with its electrons it is at some part of its path losing potential energy. In a collision with an electron the maximum loss of potential energy will be e^2/c, where c is the minimum distance between the electron in the atom and the moving electron. If the frequency of the radiation emitted is related to this loss of energy by Planck's law, then

$$h\nu = \frac{e^2}{c},$$

i. e. ν is inversely proportional to c, so that λ the wave-length of the radiation is proportional to c. If the energy T of the electron is large compared with e^2/c, c and therefore the wave-length will differ very little from b, the perpendicular from the fixed electron on the initial direction of motion of the moving one. Let us see if this will lead to the result that the probability of the emission of radiation of frequency between ν and $\nu+d\nu$ is proportional to

$$\frac{1}{\mathrm{T}} \cdot \frac{d\nu}{\nu}.$$

The probability of an electron making a collision such that b is between b and $b+db$ is proportional to $2\pi b \,.\, db$.

If $\mathrm{F}(\mathrm{T}\,.\,b)$ is the probability that this collision results in the emission of a quantum of radiation $\mathrm{F}(\mathrm{T}\,.\,b)2\pi b\,db$ must be proportional to

$$\frac{1}{\mathrm{T}}\frac{d\nu}{\nu}.$$

Since ν varies as $1/b$, $\mathrm{F}(\mathrm{T}\,.\,b)$ must be proportional to

$$\frac{\cdot 1}{\mathrm{T}b^2}.$$

Now the energy transferred at the collision between two electrons is

$$\mathrm{T}\Big/\left(1+\frac{b^2\mathrm{T}^2}{e^4}\right),$$

or when T is large compared with e^2/b, to $e^4/\mathrm{T}b^2$. Thus the chance of a quantum being emitted is proportional to the energy lost by the electron in the collision.

It follows from this way of looking at the question that there will be a maximum value of λ, for when b is large compared with the distance between the electrons in the atoms, the electric field through which the electron passes will not be the field due to a single electron, but one due to the action of several electrons and the positive charge. The electric field of the electron passing outside the atom will be the "stray" field of the atom, and the variations in the potential energy in this field may be very much less than e^2/b, where b is the distance from the atom. Thus when b exceeds a value comparable with the radius of the atom very little energy will be transformed into radiation.

There will in the discharge-tube be a continuous degradation of the primary Röntgen radiation into secondary, tertiary, and so on, radiation of longer wave-length. For the primary radiation produced by the cathode rays will be a continuous spectrum with a fixed limit; this radiation when absorbed by the gas will cause it to emit electrons covering a wide range of speeds, but none having a speed exceeding that of the original cathode rays. These secondary electrons will give rise to trains of secondary Röntgen radiation, these trains will be continuous spectra, but the limiting frequency will in each case be less than that for the primary radiation. Supposing there was no loss of energy in this process, the energy in the secondary radiation would be concentrated into a shorter range of frequencies than the primary radiation. If the secondary radiation were by a similar process converted into tertiary radiation, the range of frequencies in the tertiary radiation would be less than that in the secondary, and so on. Thus these transformations would all result in the continuous Röntgen-ray spectrum getting shorter and shorter and more and more energy being concentrated in the region of the longer wave-lengths.

We have left out of account the effect of collisions with other electrons on the energy of the electrons ejected by the radiation; if the energy of these electrons was greater than the mean energy of electrons at the temperature of the enclosure, the ejected electrons would on the whole lose some of their energy before giving rise to the secondary radiation. This would tend still further to increase the wave-length of the secondary radiation in comparison with that of the primary and so increase the rate at which radiation of a shorter wave-length than that of the mean wave-length corresponding to the temperature of the enclosure was degraded into radiation of a longer wave-length. On the other hand, if the wave-length of the primary radiation were longer than the mean, the electrons it ejected would have less energy than the average of that of the electrons in the enclosure; collisions with these electrons would increase their energy and this would diminish the wave-length of the secondary radiation. By this process the wave-length of the secondary radiation might be diminished below that of the primary. We see from this that there are agencies at work to increase the wave-length of the short radiations and diminish those of the long ones, and those bring about a distribution of wave-lengths in statistical equilibrium.

A stream of homogeneous radiation of frequency ν ejects electrons with energies equal to $h\nu$, and these electrons will give rise to a continuous spectrum of Röntgen rays where the upper limit of the frequency is equal to that of the primary beam. This secondary system will give rise to other systems whose average wave-length is greater than its own. Thus the homogeneous primary beam will be accompanied by a continuous spectrum of radiation, the wave-length of the radiation increasing with the distance from the primary beam. The time taken for the transformation of the corpuscular radiation excited by the primary Röntgen rays into the continuous Röntgen spectrum will be inversely proportional to the velocity of the ejected electrons, which will, except for very hard primary rays, be small compared with the velocity of light. Thus the primary beam will travel through a considerable distance before the transformation is completed, so that the tail will be a very long one. This continuous spectrum would constitute scattered radiation, distinct from the normal type of scattered radiation which is not accompanied by a preliminary transformation of the primary Röntgen radiation into corpuscular radiation. The latter will be of the same frequency as the primary radiation, whereas the new radiation will form a continuous spectrum with the frequency of the incident radiation as the upper limit of its frequency. Again, the variation of the intensity of the scattered radiation with the angle between the incident and scattered rays will not be the same in the two cases.

Summary.

An account is given of experiments on the radiations inside a closed vessel containing gas at a low pressure through which an electric discharge is passing. It is shown that, when electrons pass through gases, Röntgen rays are produced which may be of far higher frequency than any of the characteristic radiation of the gas. Thus, when electrons produced by a potential difference of 1500 volts passed through hydrogen, Röntgen radiations having a frequency corresponding to 1500 volts were found, The spectrum appears to be a continuous one with its maximum frequency proportional to the energy of the electrons. Some of this radiation is absorbed by gases with remarkable rapidity ; thus, for example, radiations were detected in the tube which were absorbed in 2 or 3 cm. of air at the pressure ·01 mm. of Hg. Absorption as great as this shows that the volume in which the energy of this type of radiation is concentrated must be considerably larger than the volume of a molecule of the gas. It is shown that there is some regular reflexion of the radiations from a polished metal surface, the maximum amount of reflexion obtained being about five per cent.

An expression is arrived at for the distribution of energy in the continuous spectrum produced when electrons pass through a gas.

I have much pleasure in thanking my assistant, Mr. Everett, for the help he has given me in making these experiments.

LXXXIII. *The Theory of the Drift of Projectiles.*

By E. T. Hanson, *B.A.**

Introduction.

THE investigation of the motion of a spinning shell through the air is not only of great practical importance, but also of considerable theoretical interest. The complete treatment is very difficult, and there are still many parts of it that require further investigation. The whole problem is very fully and ably treated in "The Aerodynamics of a Spinning Shell," Phil. Trans. ser. A, vol. ccxxi., by Messrs. Fowler, Gallop, Lock, and Richmond.

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* Communicated by the Author, who is indebted to the Admiralty for permission to publish this paper.

In the present short communication an extension of the Particular Integral of the approximate equations of motion is discussed. The shell is considered to be a rigid spinning body acted upon by three forces at right angles to one another passing through the centre of gravity, and by three couples about axes at right angles to one another which intersect at the centre of gravity. The problem cannot be solved generally; approximate solutions only can be obtained by certain simplifying assumptions.

Now there is one assumption about the legitimacy of which there can be little doubt. A projectile is symmetrical about its axis of spin. When it is travelling "nose on," that is when the axis is tangential to the path of the centre of gravity or, in other words, when the "Yaw" is zero, the motion of the projectile is that of a particle under the combined forces of gravity and "drag." Excepting the couple tending to reduce the spin, which couple is usually very small, all the remaining components of the force system vanish with the yaw.

Instead of putting any restrictions upon the force system called into play by the reaction of the air, the following conditions are assumed to be satisfied:—

(*a*) The spin is large or, as will be explained, sufficiently large to justify the approximations involved.

(*b*) The yaw, which is the angle made by the axis of the shell with the tangent to the path of the centre of gravity, is always small.

(*c*) The deviation of the path of the centre of gravity from the plane normal trajectory is always small.

While keeping the force system as general as possible, the initial velocity of the shell is considered to be largely arbitrary. The theory is interesting as indicating the nature of the changes produced in the drift as the spin of the shell is gradually increased without limit.

The plane trajectory is defined as the path described by the shell in space when it is treated as a particle.

Theoretically, the foregoing conditions are merely assumptions, but practically it is not too much to say that, unless they are justified, the trajectory would be in most cases useless in actual gunnery. With regard to the spin, its magnitude is dependent upon the rifling of the gun, and therefore largely controllable.

In the case of the yaw, the condition (*b*) is certainly complied with in practice, when the shell is initially stable, at all points of every trajectory which does not exceed an initial elevation of about 45°. The formula for the drift of a shell has been shown to depend very approximately upon the ratio of two of the components of the force system. But this result depends upon experimental evidence as to the magnitude of the forces, which indicates that the ratio is small. It is not a consequence of the conditions laid down above. Assuming these conditions only, it is shown under what circumstances this ratio must be small. Those cases are then considered in which it is possible to treat the components of the force system very generally. An apology must be made for treating the notation somewhat carefully in the next section. Much difficulty is often caused by lack of appreciation of this important detail.

The Force System and Coordinate System.

Let O be the centre of gravity of the shell, and OXYZ a system of rectangular coordinates. Let OY be the direction of motion of the centre of gravity at any instant, and let XOY be the plane which contains the axis of spin initially, so that the angular precession is measured from XOY. Let OB be the direction of the axis of spin at any instant. Then the angle BOY is the yaw of the shell. The angle which the plane BOY makes with XOY is the angle of precession.

Let BOY $=\phi$

and let the angle of precession $=\psi$.

Let OA be perpendicular to OB and in the plane BOY, which is the plane of yaw. Let OC be perpendicular to OA and OB. Let OA′ and OC′ be the positions which OX and OZ would respectively take up if they were rotated about OY through an angle ψ.

The force system due to air resistance is then defined as follows:—

The drag R acting along YO.

A force $R_1 \sin\phi$ acting along OA′.

A force $R_2 \sin\phi$ acting along OC′.

A couple M acting about OB and tending to reduce the spin.

A couple $M_1 \sin\phi$ acting about OA, tending to turn OB into the position OC.

A couple $M_2 \sin\phi$ acting about OC, tending to turn OB into the position OA.

$R_1R_2M_1M_2$ being quite arbitrary, the factor $\sin\phi$ is justified by the assumption that these forces vanish with ϕ. Through O construct a plane perpendicular to the plane trajectory and cutting the latter in G. Let OY′ be parallel to the tangent at G in the direction of travel, and let OX′ be parallel to the normal at G drawn outwards. Let OZ′ be drawn to the right of the plane trajectory. Let the plane XOY cut the plane Y′OZ′ in OW. In order to make the foregoing systems of reference quite precise, it is only necessary to adopt the following convention :—

As the centre of gravity moves, the plane XOY always contains OX′.

Let the angle $Y'OW = \alpha$ and $YOW = \gamma$.

Let OX′ make with the vertical an angle θ. Since α and γ are assumed to be small, α is the deviation of the direction of motion of the centre of gravity from the tangent to the plane trajectory to the right, and γ is the deviation upwards. Let the velocity of G along the plane trajectory be noted by v. To the approximation required this is the velocity of O. Let Ω be the spin of the shell, m its mass and C its moment of inertia about its axis of spin.

The Equations of Motion.

When a shell leaves the muzzle of a gun, the motion of its axis is frequently of a highly oscillatory character. The initial values of $\dot{\phi}$ and $\dot{\psi}$ may be such as to set up rapid vibrations of period comparable with that of the spin. These vibrations take place about a mean steady motion of the axis, which is comparatively slow. This mean steady motion gives rise to the trajectory, which is known as the "mean twisted trajectory."

The approximate theory of these vibrations has been dealt with in various places, and there is evidence to show that they gradually subside. It is not intended here to consider the theory of these oscillations under a completely general force system, but it is assumed that the initial values of $\dot{\phi}$ and $\dot{\psi}$ are such that the shell describes its mean twisted trajectory, without oscillations of its axis, from the moment when it is clear of the muzzle blast. These are, in fact, the conditions usually selected for the "particular integral" of the approximate equations of motion. Under these circumstances $\dot{\phi}$, $\dot{\psi}$, and, of course, $\dot{\theta}$ may all be considered small compared with Ω.

The general equations of motion have been fully dealt with elsewhere. In the present notation, except for the force system, they are given in a paper entitled "The Initial Motion of a Projectile" (Phil. Mag. xlvi. p. 1027). Under the conditions here laid down the last two of equations (8) of that paper reduce to

$$\left.\begin{aligned} -C\Omega\Omega_2&=M_1 \\ \text{and} \qquad C\Omega\Omega_1&=M_2 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

With regard to the validity of these equations, they theoretically imply little restriction upon the force system, assuming that we may make the spin as great as we please. The value of $\dot{\phi}$ may be initially large, but the greater it is initially the more rapidly is it damped out (see equation 8 below). The force components upon which $\dot{\psi}$ depends must be kept within limits, and in fact they are in practice small enough to justify the application of (1) in the derivation of the approximate formula for drift.

These two equations (1) combine into the single complex equation

$$\left.\begin{aligned} \frac{\partial}{\partial t}(\phi e^{i\psi})+\dot{\theta}+\gamma+i\dot{\alpha}&=-\kappa\phi e^{i\psi}, \\ \text{where} \qquad \kappa&=\frac{M_1-iM_2}{C\Omega} \end{aligned}\right\} \quad . \; . \; . \quad (2)$$

The equations (4) and (5) of the same paper, when reduced, combine into

$$\left.\begin{aligned} \dot{\gamma}+i\dot{\alpha}-\frac{g}{v}\sin\theta(\gamma+i\alpha)&=f\phi e^{i\psi}, \\ \text{where} \qquad f&=\frac{R_1-iR_2}{mv} \end{aligned}\right\} \quad . \; . \; . \; . \quad (3)$$

The slightly altered notation and generalization of the force system require no further explanation.

The Solution of the Equations.

It is convenient to write

$$\phi e^{i\psi}=p \quad \text{and} \quad \gamma+i\alpha=q.$$

The equations (2) and (3) then become

$$\dot{p}+\kappa p+\dot{\theta}+\dot{q}=0, \quad . \; . \; . \; . \; . \; . \quad (4)$$

$$\dot{q}+\tan\theta\,.\,\dot{\theta}q-fp=0, \quad . \; . \; . \; . \; . \; . \quad (5)$$

making use of the well-known equation of the plane trajectory

$$\dot{\theta}=-\frac{g}{v}\cos\theta.$$

Under the conditions laid down, the formulæ (4) and (5) are quite general.

Since $$\tan\theta\,.\,\dot{\theta}=-\frac{g}{v}\sin\theta,$$

equation (4) may be written

$$\dot{p}+(\kappa+f)p-\frac{g}{v}\cos\theta+\frac{g}{v}\sin\theta\,.\,q=0. \quad . \quad . \quad (6)$$

Now let us consider trajectories whose initial elevations do not exceed 45°. These are sufficient for our purpose, and it will be shown that they can be treated with considerable accuracy and simplicity. There is no justification for omitting $\dot{q}$ in (4), for over a large part of most trajectories $\dot{q}$ may be quite comparable with $\dot{\theta}$ without contravening condition (*c*). This latter condition requires that q should be small, and therefore, initially, the last term of (6) will be small compared with the penultimate term. But since $\sin\theta$ decreases and $\cos\theta$ increases until the vertex is reached, we have an additional justification for assuming that the last term is entirely negligible in its effect upon the yaw.

The equation (6) may therefore be written

$$\dot{p}+(\kappa+f)p+\dot{\theta}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The complementary function is obtained by omitting $\dot{\theta}$. It is

$$p=\phi e^{\iota\psi}=\phi_0 e^{-\int(\kappa+f)dt}, \quad . \quad . \quad . \quad (8)$$

if the initial values of ϕ and ψ be ϕ_0 and zero respectively. The complementary function is, therefore, damped out, and is also oscillatory in character. When substituted in (5) it results in the "mean twisted trajectory" and produces no permanent drift.

The particular integral can be written

$$p+\frac{\dot{\theta}}{\kappa+f}+\frac{\ddot{\theta}}{(\kappa+f)^2}-\frac{\dot{\theta}(\dot{\kappa}+\dot{f})}{(\kappa+f)^3}+\ldots\ldots=0.$$

Now $\ddot{\theta}$ is always very small, and the rate of change of the force system is taken to be never large. Hence, if one of the components of κ or f be moderately large, the third and remaining terms of this expression are quite negligible.

Hence for the particular integral we have

$$p=-\frac{\dot{\theta}}{\kappa+f}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Substituting (9) in (5), we obtain

$$\frac{\partial}{\partial t}\{q\sec\theta\} = -\frac{f}{\kappa+f}\sec\theta\,.\,\dot{\theta}, \quad . \quad . \quad . \quad (10)$$

for it is unjustifiable to assume here that $\dot{\theta}q$ is negligible.

If f be large compared with κ, the factor $f/(\kappa+f)$ may be treated as sensibly constant. In any case, if this factor be constant the equation can be completely solved.

The solution required can be expressed in the form

$$\dot{q} = \frac{f}{\kappa+f}\dot{\theta}\left[\sin\theta\log\tan\left(\frac{\pi}{4}+\frac{\theta}{2}\right)-1\right]. \quad . \quad . \quad (11)$$

Hence at the vertex

$$\dot{q} = -f\dot{\theta}/(\kappa+f),$$

and therefore, unless f be small compared with κ, the condition (c) will not be satisfied.

If, on the other hand, f is small, we may write (10) in the form

$$\frac{\partial}{\partial t}(q\sec\theta) + \frac{f}{\kappa}\sec\theta\,.\,\dot{\theta} = 0. \quad . \quad . \quad . \quad . \quad (12)$$

In practice the only components which need be retained are M_2 and R_1, so that

$$\frac{f}{\kappa} = i\frac{R_1}{M_2}\cdot\frac{C\Omega}{mv}.$$

In this case (12) is equivalent to Mayevski's equation for drift in its generalized form.

Considering now those cases in which $\dot{\theta}$ is small, of the same order as $\dot{q}$, (5) may be written

$$\dot{q} - fp = 0,$$

so that, from (9),

$$\dot{q} = -\frac{f}{\kappa+f}\dot{\theta}.$$

This equation may easily be discussed generally, but for convenience and brevity consider, as before, only the components M_2 and R_1, and let the ratio R_1/M_2 be constant.

Let $f=\rho$ and $\kappa=-i\mu$, and note that ρ/μ is proportional to the spin.

Then

$$\dot{\gamma} = -\frac{\rho^2}{\mu^2+\rho^2}\dot{\theta}$$

and

$$\dot{\alpha} = -\frac{\mu\rho}{\mu^2+\rho^2}\dot{\theta}.$$

If the ratio ρ/μ be treated as a variable parameter, then, for a given point on the trajectory, γ will increase continuously from 0 to $\theta_0-\theta$ as ρ/μ increases from 0 to infinity. Under the same circumstances α will increase from 0 to a maximum $\frac{1}{2}(\theta_0-\theta)$, and will then decrease to zero. This maximum occurs when the ratio ρ/μ is unity.

Thus under no circumstances can the vertical drift do more than counteract the effect of gravity, nor can the lateral deviation exceed half the maximum value of the vertical deviation. Only when the ratio ρ/μ is less than unity can the lateral deviation exceed the vertical.

LXXXIV. *The Flow of Water in an Inclined Channel of Rectangular Section.* By HAROLD JEFFREYS, *M.A., D.Sc., Fellow and Lecturer of St. John's College, Cambridge*[*].

1.0. IT is well known that water flowing in pipes obeys the laws of viscous flow so long as the velocity does not exceed a certain limit depending on the viscosity and on the dimensions of the pipe, but that if the velocity exceeds this limit the motion ordinarily becomes turbulent and the frictional stress becomes proportional to the square instead of the first power of the velocity. The corresponding problems relating to the flow of a fluid over a plane seem to have received much less attention from the experimental side, though it is generally believed that the laws followed are very similar. The frequent occurrence in nature of turbulent flow over a plane or nearly plane surface, with a free surface for the upper boundary, suggested that a direct experimental determination of the coefficient of skin friction and of the Reynolds criterion for turbulence in such a case was desirable. Such an investigation is described in the following pages. A determination of the Reynolds criterion in similar conditions has been previously made by L. Hopf[†], but he did not find the coefficient of skin friction when the critical speed was much exceeded, and the methods adopted differ materially in the two cases.

2. THEORY.

2.1. *Purely viscous flow.*—Let α be the inclination of the surface to the horizontal, and let axes of x and z be taken, x along the direction of greatest slope and z perpendicular to the plane. Let u be the velocity, ζ the depth, and ν the kinematic viscosity. Then if the channel be of uniform width, we have the dynamical conditions

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[*] Communicated by the Author.

[†] *Ann. d. Phys.* (4) xxxii. pp. 777–808 (1910).

$$\frac{du}{dt}=g\sin\alpha-\frac{1}{\rho}\frac{\partial P}{\partial x}+\nu\frac{\partial^2 u}{\partial z^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$0=-g\cos\alpha-\frac{1}{\rho}\frac{\partial P}{\partial z}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P denotes the pressure and g the intensity of gravity. The vertical acceleration has been neglected, since it is essentially an insignificant fraction of g. We have, further, the equation of continuity

$$\frac{\partial\zeta}{\partial t}=-\int_0^\zeta\frac{\partial}{\partial x}(u\zeta)\,dz. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In steady flow (3) is an identity, and (2) shows that so long as $\partial\zeta/\partial x$ is not comparable with $\tan\alpha$, the pressure term can be omitted from (1). This being the typical case, the solution of (1) must be

$$u=\frac{g\sin\alpha}{2\nu}(2z\zeta-z^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since this satisfies the boundary conditions, namely that u is zero in contact with the bottom, where z vanishes, and that $\partial u/\partial z$ is zero at the surface. The surface velocity is

$$u_1=g\sin\alpha\,.\,\zeta^2/2\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the mean velocity, taken with regard to the depth below the surface, is

$$u_0=g\sin\alpha\,.\,\zeta^2/3\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that the mean velocity is necessarily 2/3 of the surface velocity.

The rate of flow of fluid across a unit length perpendicular to the direction of flow is

$$Q=u_0\zeta=g\sin\alpha\,.\,\zeta^3/3\nu. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If then Q and ν are specified, the depth and the velocity at any depth are determinate. Conversely, if we can measure Q and u_1 or ζ, we can find ν.

2.2. *Turbulent flow.*—With the same notation, save that u will be taken to denote the mean velocity at the depth under consideration (*i. e.*, eddy velocities are supposed averaged out), let the frictional force per unit area over the bottom be $\kappa\rho u_1^2$, where ρ is the density and κ the numerical constant of skin friction. The condition for the water to be unaccelerated is that

$$\kappa u_1^2 = g\zeta \sin\alpha. \qquad (1)$$

The ratio of the mean velocity to the surface velocity is subject to some uncertainty. If it be m, we have

$$Q = mu_1\zeta = m(g \sin\alpha \,.\, \zeta^3/\kappa)^{\frac{1}{2}} \qquad (2)$$

$$= m\kappa u_1^3/g \sin\alpha. \qquad (3)$$

If m be known, a determination of Q and of u_1 or ζ will enable us to find κ.

In turbulent flow there is always a region of laminar flow with rapid shearing close to the solid boundary. If the velocity at the boundary between the turbulent and non-turbulent regions is nu_1, and if the thickness of the non-turbulent region is l, which is by hypothesis small compared with ζ, the conditions at the solid surface are:

$$u = 0, \qquad (4)$$

$$\nu \frac{du}{dz} = \kappa u_1^2. \qquad (5)$$

If then l be so small that we can neglect l^2d^2u/dz^2, we have

$$\nu n u_1/l = \kappa u_1^2,$$

that is

$$l = \nu n/\kappa u_1. \qquad (6)$$

Again, let us suppose that the conditions in the turbulent layer can be represented by a uniform coefficient of eddy viscosity k. Then within this layer we must have

$$u = u_1 - \frac{g \sin\alpha}{2k}(\zeta - z)^2, \qquad (7)$$

so that

$$(1-n)u_1 = g \sin\alpha \,.\, \zeta^2/2k, \qquad (8)$$

with our approximations. The mean velocity in the turbulent layer is $(\frac{2}{3}+\frac{1}{3}n)u_1$, and that in the non-turbulent layer is $\frac{1}{2}nu_1$. Thus the mean velocity over the whole depth is given by

$$mu_1\zeta = (\zeta - l)(\tfrac{2}{3}+\tfrac{1}{3}n)u_1 + l \,.\, \tfrac{1}{2}nu_1, \qquad (9)$$

so that practically

$$m = \tfrac{2}{3}+\tfrac{1}{3}n. \qquad (10)$$

A determination of the velocities at the surface and at the boundary of the non-turbulent layer will therefore give the mean velocity. Further, we have from (8) and (1)

$$2k = \frac{g \sin \alpha \, . \, \zeta^2}{(1-n)u_1} = \frac{\kappa^2 u_1^3}{(1-n) g \sin \alpha}$$

$$= \frac{\kappa Q}{m(1-n)} \quad . \quad . \quad . \quad (11)$$

by (3).

Thus the eddy viscosity is determinate. Again, we readily see from (6) that the smallness of l/ζ requires that Q/ν shall be large compared with nm/κ. If this condition is not satisfied, the non-turbulent layer will take up a considerable part of the depth of the liquid, and an important correction will be needed to allow for it.

2.3. *The Reynolds number.*—It can as usual be shown from dynamical similarity that the resistance to the motion of a fluid over a plane must be of the form

$$F = \kappa \rho u_1^2 . f(Q/\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The no-dimensional parameter Q/ν will here be used as the Reynolds criterion. It has the advantage that both Q and ν are directly under control, the former by regulating the supply of water, the latter by varying the temperature or the amount of dissolved material.

When Q/ν is very great, f is practically unity; when it is small, we easily find from 2.1 that

$$f\left(\frac{Q}{\nu}\right) = \frac{4}{3} \frac{\nu}{\kappa Q} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The form of this suggests that the transition from purely viscous to turbulent motion will take place when Q/ν is in the neighbourhood of $4/3\kappa$. The transition need not, however, be sudden.

3. EXPERIMENT.

3.1. I am much indebted to the courtesy of Prof. Inglis for being allowed to carry out the following experiments in the Hydraulics Department of the Cambridge Engineering Laboratory, and to Mr. R. R. M. Mallock for the loan of an instrument for producing a steady flow of liquid.

3.2. The flow investigated was produced in a wooden trough 364 cm. long, 10·2 cm. wide, and 5 cm. deep, all measurements being internal. The upper end was closed and the lower open, and the whole was painted. The heights of the ends of the trough above the bed could be adjusted by means of blocks. The water-supply was taken from a tank designed to maintain a constant head, and before it entered the trough it was made to pass through Mr. Mallock's device for reducing irregularities of flow. In this it first percolated through a number of holes in a brass plate and then ran over two weirs and finally down a smooth metal ledge into the head of the trough. Except at the very lowest speeds, when it was difficult to keep the whole of the ledge wet, the water entered the trough in a uniform thin sheet whose width was nearly that of the channel.

To determine ν or κ it was necessary to measure two of the three quantities Q, u_1, and ζ. The first offered no difficulty; it was sufficient to measure the total rate of supply of water by observing the time needed to fill a 2000 c.c. measuring jar, and then to obtain Q by dividing the flow per second by the breadth of the trough. The depth of the water was much more difficult to find. Had the surface been actually a plane, it might have been done by placing a bar of square section across the top of the trough and then measuring down to the bottom and to the free surface by means of a steel scale. The surface, however, was always covered with waves. The most conspicuous were standing waves, spreading like ship-waves from places at the edges where the film raised by surface tension had dried. These could be considerably reduced for a short time by running the hand along and re-wetting the sides. In addition there were usually progressive waves, apparently of greater amplitude, but more difficult to see on account of their speed. On account of the two types of waves, it was impossible to be confident that measures of the depth could be trusted within a millimetre; since the total depth was usually only about 5 mm., and since it would have to be cubed in the calculation, this method was abandoned. Hopf comments on the difficulty of measuring the depth, but seems to have succeeded better than I did.

I therefore resorted to measuring u_1 by observing the time it took a recognizable object to pass through a known distance. At first, pieces of paper about 1 cm.^{2} in area were dropped in at 50 cm. from the head of the trough and timed over the remaining 314 cm. This method usually worked well, except when the depth was small, when the paper was liable to drag on the bottom; it was easy to see when this was happening, but it led to the rejection of a considerable number of observations. It proved to be more convenient to observe a drop of ink; the front of a patch of ink gave a measure of the velocity at the surface which agreed satisfactorily with the results found with paper.

The critical Reynolds number, corresponding to the lowest value of Q that makes the flow turbulent, was found by dropping ink into the water. In viscous flow the ink was drawn out into a thin line, save for a faint uniformly tinted patch left on the surface, probably by some surface tension effect. In turbulent flow the front of the inky patch was speckled, not uniform, but shaded behind into a long region where the tint seemed to vary continuously. The ink used was for the most part a blue-black fountain-pen ink. Its density was considerably greater than that of water. A red ink, made up to the density of water by the addition of a little methylated spirit, was also used, but showed no systematic difference; probably in both cases the mixing when the ink was added was sufficiently thorough for the difference of density to be unimportant.

It was important that the length of the trough should be along the lines of steepest slope of the bottom; in other words, that lines of the bottom perpendicular to the sides should be level. Otherwise the water flowed down one side, and too low results were obtained for the viscosity or the skin friction coefficient.

If Q and u_1 are observed, we can calculate ν or $m\kappa$ from the formulæ

$$m\kappa = \mathrm{Q}g \sin\alpha / u_1^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\nu = \frac{9}{8} \frac{\mathrm{Q}^2 g \sin\alpha}{u_1^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The results in the table are arranged in order of ascending values of Q; $m\kappa$ and ν have been calculated separately for each set of observations.

It is seen that the first three values of ν found from the experiment are approximately equal to the true viscosity of water. The correct values found from the tables for water at the actual temperatures are 0·0131, 0·0119, and 0·0115. For these rates of supply the flow was therefore presumably entirely or almost entirely laminar. For all other values of Q, however, the value of ν found from formula (2) was much greater than the true viscosity; the motion was therefore turbulent. Omitting then the first three entries, we can use the remaining 21 to find $m\kappa$. The frequency distribution of the various values of 1000 $m\kappa$ is as follows:—1·7 to 1·9, 2; 1·9 to 2·1, 2; 2·1 to 2·3, 6; 2·3 to 2·5, 3; 2·5 to 2·7, 3; 2·7 to 2·9, 4; 2·9 or more, 1. The arithmetic mean is 2·38, and the standard deviation 0·31. Hence the probable error of the arithmetic mean is 0·05. Thus the product $m\kappa$ is $0{\cdot}00238 \pm 0{\cdot}00005$.

Q. cm.^{2}/sec.	u_1. cm.^{2}/sec.	cosec α.	ν. 10^{-2} cm.^{2}/sec.×.	$m\kappa$. 10^{-3}×.	n.
2·97	32·9	22·3	1·20	3·68	
3·46	37·5	24·3	1·03	2·65	
4·29	45	22·2	1·01	2·08	
6·35	50	22·3	1·60	2·24	
7·35	68	12·3	1·54	1·87	
7·46	53	24·3	1·66	1·99	
7·60	58	22·3	1·75	2·05	
12·6	48	43	3·68	2·60	
12·6	73	12·3	......	2·58	
13·7	60	24·3	......	2·57	0·87
16·4	68	22·3	......	2·28	0·77
17·8	65	22·3	......	2·87	0·75
18·6	67	22·2	......	2·73	0·84
18·9	87	12·3	......	2·28	
18·9	95	7·9	......	2·75	0·81
18·9	70	23·0	......	2·33	
22·2	71	22·2	......	2·75	0·88
26·7	79	22·2	......	2·38	0·82
31·3	85	22·2	......	2·26	0·87
37·6	83	22·3	......	2·90	
40	131	7·35	......	2·38	
40	106	15·6	......	2·12	
40	61	69	......	1·74	
40	103	15·6	......	2·30	

The chief factor in producing the deviations from the mean value is the inaccuracy of the velocity. The observed time of transit of the water along the trough was on an average about five seconds. It was measured with a stop-watch graduated to fifths of a second. Each reading was repeated several times, and as a rule the observations differed among themselves by one or two fifths of a second. Thus the probable error of the velocity is comparable with 4 per cent. It is cubed in the calculation, giving an error of 12 per cent. in $m\kappa$. This is nearly equal to the standard deviation of the determinations. Q and α can hardly be in error by more than 1 or 2 per cent. A more accurate way of determining the velocity may therefore lead to a considerable reduction in the outstanding probable error.

3.3. *Determination of* m.—When the velocity was found by means of ink drops, the front and the back of the inky patch in the water were, as a rule, both timed along the trough. It seems reasonable to suppose that eddies distributed the ink vertically throughout the turbulent layer. If any ink entered the non-turbulent layer, however, it would be extended so rapidly lengthwise as to become very much fainter than the ink in the turbulent layer. Hence in turbulent motion the back of the inky patch would be expected to correspond to the velocity at the transition between the turbulent and non-turbulent layers. On this assumption, the value of n is given in the table. The mean value is $0{\cdot}83 \pm 0{\cdot}02$. Hence, by 2.2 (10), m is $0{\cdot}94 \pm 0{\cdot}01$. Thus κ is $0{\cdot}00253 \pm 0{\cdot}00006$.

3.4. *The critical Reynolds number.*—With the trough at inclinations of 1/15 and 1/23, drops of ink were added to find out whether the motion was in fact turbulent or not; in each case it was found that turbulence set in when Q was about 3·8 cm.^{2}/sec. The temperature was 12°·4, making the viscosity 0·0123 cm.^{2}/sec. Thus the critical Reynolds number was about 310.

Hopf gets 300 to 330 by a different method. He finds ν by a formula equivalent to 3.2 (2). It remains constant for values of Q up to a certain limit, and then begins to increase nearly linearly with Q. This limit is taken to give the critical Reynolds number.

Up to this value the motion is purely viscous, and the mean velocity is 2/3 of the surface velocity. Above it, the vertical extent of the turbulent region generally increases and the ratio at the same time rises.

It was seen in 2.3 that the two laws of fluid friction became equivalent when the Reynolds number was $4/3\kappa$, which we now find to be 530. There must therefore be a gradual transition from one law to the other, not a sudden change from a linear law to a square law when Q/ν reaches 310.

3.5. *The eddy viscosity.*—If we use 2.3 (11), with the values found for n and κ, we have in general

$$k = 0{\cdot}0080\,Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This result depends only on the hypotheses that the supply of fluid is much above the critical Reynolds value and that k is the same at all distances below the surface. It might vary on account of variation in n, but such variation seems unlikely to be great. If it occurred it would probably act in the direction of making the top more independent of the bottom at the higher speeds; thus n might diminish. Even, however, if n became zero, k would only change to $\frac{3}{4}\kappa Q$ or $0{\cdot}00192\,Q$. The order of magnitude of k therefore seems to be fixed in any case. With the largest value of Q used in these experiments, namely 40 cm.^{2}/sec., k is found to be 0·32 cm.^{2}/sec.

3.6. *The non-turbulent layer.*—When the rate of flow was only two or three times the critical rate, a drop of ink placed in the stream penetrated into the turbulent layer and was drawn out into a long straight filament by the shearing in that layer. The ink that stayed in the turbulent layer naturally became diffuse and rushed ahead. With greater rates of flow the non-turbulent layer became thinner, and it became more difficult to make it visible. Merely injecting ink into the stream in the neighbourhood of the bottom did not produce the desired effect. Probably the action of forcing ink into the water in itself introduced a certain amount of turbulence locally, and the turbulent fluid immediately mixed with the turbulent layer and was carried away. When a larger amount of ink, say 0·5 c.c., was projected nearly normally at the bottom, more success was obtained. A little of it in this case became entangled in the non-turbulent layer. With the highest values of Q and α used, corresponding to a velocity of over a metre a second, some ink injected in this way could be seen several seconds afterwards, advancing in a stream-line motion with a velocity about 1 per cent. of that at the surface.

4. COMPARISON WITH RELATED RESULTS.

The value found for the coefficient of skin friction, namely 0·00256, may be compared with those found by G. I. Taylor[*] from observations of wind at various heights, namely 0·0023 for light, 0·0032 for moderate, and 0·0022 for strong winds. The two problems refer to somewhat different conditions, however. In the air there is an almost permanent tendency to stability, owing to the difference between the actual and the adiabatic lapse-rates of temperature with height; this is absent from the present problem. Further, my formula expresses the skin friction in terms of the velocity of the water at the free surface; Taylor's expresses it in terms of the velocity at the lowest level recorded by a pilot balloon, whereas the meteorological analogue of the velocity at the free surface is probably the geostrophic wind. Thus the numerical agreement between my coefficient and Taylor's, beyond the order of magnitude, is accidental.

In work on tidal friction in shallow seas, Taylor and I took the coefficient of skin friction in tidal currents to be 0·002, the surface velocity being used as the datum; the results of this paper indicate a coefficient about 25 per cent. greater.

In hydraulics, computations for conduits are usually based on the Chézy formula, which in the notation used here is equivalent to

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[*] Proc. Roy. Soc. A, xcii. pp. 196–199 (1916).

$$mu_1 = \mathrm{C}(\zeta \sin \alpha)^{\frac{1}{2}},$$

C being the Chézy coefficient. Comparing with 2.2 (1), we have

$$\kappa = m^2 g/\mathrm{C}^2.$$

The Chézy coefficient in metre-second units, with an unplaned plank bottom, when the water is shallow in comparison with its width, is about 55 [*]. With this value, and our value of m, we find that κ is 0·00286. For a neat cement bottom C is 64, making κ equal to 0·00221. It may be remarked, however, that the smallest depth given in the table quoted corresponds to a value of Q of 880 cm.^{2}/sec., whereas those in my experiments ranged from about 3 to 40 cm.^{2}/sec. On the other hand, much experimental evidence is harmonized if we suppose that κ is really proportional [†] to $(\nu/\mathrm{Q})^{\frac{1}{4}}$, so that a value of κ of 0·0022, for Q equal to 880 cm.^{2}/sec., would correspond to one of 0·0045, for Q equal to 40 cm.^{2}/sec. In that case my lower values will have to be attributed either to the greater smoothness of the bottom or to a departure of friction for moderate values of Q from the law appropriate to large values.

Merriman, who follows Bazin, quotes higher values of C for greater depths, but this is probably due in part to edge effects. On the other hand, lower values of C, ranging down to 17, are given for other types of bottom, the lowest referring to weeds. The theory of the effect on the skin friction of variations in the nature of the bottom is likely to be rather difficult. So long as the projections on the bottom are small compared with the thickness of the non-turbulent layer, and so long as the fluid wets the bottom, it seems unlikely that they can affect the friction appreciably. A slight confirmation of this may be afforded by the fact that Hopf's determinations of the critical value of Q/ν for water flowing over brass and glass agree with mine for a planed plank bottom. If the projections are great enough to penetrate the non-turbulent layer, however, they may affect the character of the turbulence; the projections, by obstructing the current, may considerably increase the friction. Incidentally, as v. Kármán points out, they improve the accuracy of the proportionality of the friction to the square of the velocity. Weeds differ from other projections in being movable. Among the weeds the flow may be largely viscous, especially if they are growing thickly; thus they may much reduce the effective depth of the stream. It seems likely that the ratios of the height of the projections to the depth of the fluid and the thickness of the non-turbulent layer are important data relative to the law of friction in a stream.

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[*] Merriman, 'Treatise on Hydraulics,' p. 314.

[†] *Cf.* T. von Kármán, *Zs. f. ange. Math. u. Mech.* i. pp. 233 252 (1921).

In the flow of fluids in pipes turbulence usually develops when u_0a/ν reaches 1015: here u_0 is the mean velocity and a the radius. In the rectangular case, Q was practically the ratio of the rate of flow through a section to the wetted perimeter of the section; in a circular pipe this is $\frac{1}{2}u_0a$. Thus the critical value of the analogue of Q/ν is 525, instead of 310 as found for the trough. The difference may be attributed to the additional possibilities of instability introduced by the free surface. Streams in turbulent flow, however slight the wind may be, never seem to have perfectly even surfaces; the surface is always quivering, and reflects irregularly. The skin friction in pipes is about $0{\cdot}0025\,\rho u_0^2$ per unit area; if it is expressed in terms of the maximum velocity, the numerical coefficient will have to be less than in the case of a stream with a free surface.

5. PROGRESSIVE WAVES.—Reference has already been made to the presence of progressive waves on the water during the experiments. It was actually to test a theory of the formation of such waves that the experiments were originally undertaken. It has been noticed by Vaughan Cornish * that the water in certain Alpine conduits, with plane bottoms and rectangular sections, does not flow in a steady stream but in a series of waves. The height of the waves is comparable with the mean depth of the water (about 3 inches), and the velocity is appreciably greater than that of the surface of the water. It appeared possible that the development of waves of such size might be due to an essential instability of the uniform flow of a stream in certain conditions, and on investigation it is found that such instability is present in all cases when the slope of the bottom exceeds a certain definite numerical value. It is to be noticed that this instability is different in character from the instability that leads to the transition from laminar flow to turbulent flow. It presupposes that the flow is already turbulent, and indicates a transition, from the ordinary flow of a stream with a plane or nearly plane

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* 'Waves of the Sea and other Water-Waves,' pp. 294–330 (1910).

free surface, to a different turbulent flow with the surface marked by moving transverse ridges.

In the following theory the motion will be supposed thoroughly turbulent, the friction proportional to the square of the velocity, and the wave-length of the disturbance of the steady motion long compared with the depth of the fluid. As an approximation, the velocity u will be supposed the same at all depths. The equation of continuity is

$$\frac{\partial \zeta}{\partial t} = -\frac{\partial}{\partial x}(u\zeta). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The dynamical equation is obtained by integrating the equation of motion down the slope with respect to the depth, the range of integration being from the bottom to the free surface. It is

$$\zeta\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x}\right) = \left(g \sin \alpha - g \cos \alpha \frac{\partial \zeta}{\partial x}\right)\zeta - \kappa u^2. \quad . \quad (2)$$

In steady motion, let

$$\zeta = h, \quad u = \mathrm{U}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in the disturbed motion let

$$\zeta = h + \zeta', \quad u = \mathrm{U} + u'. \quad . \quad . \quad . \quad . \quad (4)$$

We have the steady motion condition :

$$gh \sin \alpha = \kappa \mathrm{U}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If for shortness we write σ for $\partial/\partial t$, and p for $\partial/\partial x$, equations (1) and (2) reduce to

$$(\sigma + \mathrm{U}p)\zeta' = -hpu', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$(\sigma + \mathrm{U}p)u' = \left(\frac{g}{h} \sin \alpha - gp \cos \alpha\right)\zeta' - \frac{2\kappa \mathrm{U}}{h}u', \quad . \quad . \quad (7)$$

where all terms depending on squares and products of the departure from steady motion have been neglected. On eliminating and using (5), we find that u' and ζ' are both annulled by the operator

$$(\sigma + \mathrm{U}p)^2 + \frac{2\kappa \mathrm{U}\sigma}{h} + 3gp \sin \alpha - ghp^2 \cos \alpha. \quad . \quad . \quad (8)$$

Any small disturbance of the steady state that may exist at first can be expressed as a combination of sines and cosines of multiples of x, or alternatively as a combination of terms of the form $e^{\iota\beta x}$, where β is purely real. Then each term of this latter type will give solutions of (8) of the form $Ae^{\gamma t+\iota\beta x}$, where A and γ are constants. A depends wholly on the initial conditions; γ is to be found by writing $\iota\beta$ for p and γ for σ in (8), equating the resulting expression to zero, and solving for γ. If the resulting value of γ has a zero or negative real part, the steady motion is stable; but if it has a positive real part, any initial small disturbance of the type considered will increase exponentially until its amplitude becomes so great that its square can no longer be neglected. We actually find on solving that

$$\gamma=-\mathrm{U}\iota\beta-\frac{\kappa\mathrm{U}}{h}\pm\left(\frac{g}{h}\right)^{\frac{1}{2}}(\kappa\sin\alpha-\iota\beta h\sin\alpha-\beta^2h^2\cos\alpha)^{\frac{1}{2}}. \quad (9)$$

Put

$$\beta h=\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

so that λ is a pure number. Then

$$\beta\mathrm{U}=\lambda\left(\frac{g\sin\alpha}{\kappa h}\right)^{\frac{1}{2}}; \quad \frac{\kappa\mathrm{U}}{h}=\left(\frac{\kappa g\sin\alpha}{h}\right)^{\frac{1}{2}}; \quad . \quad (11)$$

and

$$\gamma=\left(\frac{g\sin\alpha}{\kappa h}\right)^{\frac{1}{2}}\left[-\iota\lambda-\kappa\pm(\kappa^2-\iota\kappa\lambda-\kappa\lambda^2\cot\alpha)^{\frac{1}{2}}\right]. \quad (12)$$

It is clear from this result that, for any value of β, at least one of the associated values of γ has a negative real part; further, that if α is small enough they both have negative real parts. This corresponds to the ordinary fact of observation that waves on a stream of small slope tend to die out. The transition to instability can occur only if γ passes through a value with a zero real part. But the condition for γ to be purely imaginary is that the square root in (12) shall be of the form $\kappa+\iota\delta$, where δ is real. Expressing this equality, we derive the equation:

$$\kappa^2-\iota\kappa\lambda-\kappa\lambda^2\cot\alpha=\kappa^2+2\iota\kappa\delta-\delta^2. \quad . \quad . \quad . \quad (13)$$

Equating real and imaginary parts we have

$$\delta=-\tfrac{1}{2}\lambda; \quad \delta^2=\kappa\lambda^2\cot\alpha; \quad . \quad . \quad . \quad . \quad (14)$$

and on eliminating δ we have simply

$$\tan\alpha=4\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus the steady flow will first become unstable when the slope is just greater than 4κ, or practically 1 in 100. For the first wave that is able to grow, γ has imaginary part $\left(\frac{g\sin\alpha}{\kappa h}\right)^{\frac{1}{2}}(-\tfrac{3}{2}\iota\lambda)$. The velocity of the wave is therefore down stream and equal to $-\gamma/\beta$, or $\frac{3}{2}$U. The wave therefore travels one and a half times as fast as the water. The instability develops at the same stage for all wave-lengths, subject to the condition of the problem that the wave-length is great compared with the depth of the water.

It may be remarked that if the slope has the critical value 4κ, the velocity of the water is just equal to $2(gh)^{\frac{1}{2}}$, and the velocity of the wave will exceed that of the water by $(gh)^{\frac{1}{2}}$, which is just the velocity of a long wave in standing water. Cornish comments on the fact that the waves in his conduits seemed to gain on the water with a velocity equal to that of a wave in standing water of the same depth; it appears that the present argument is able to account for this fact, at any rate at the beginning of the formation of waves.

When waves have once begun to form, it is clear that the water of the crests will tend to rush down, gaining over the troughs, till the surface has been converted into a series of bores following one another down stream. A considerable extension of the theory would be required to give a quantitative account of the final stage. The theory as here developed deals only with the earliest stage of the development of roll-waves, and shows that they are to be expected in all rectangular conduits whose slopes exceed 1 in 100. Those described by Cornish have slopes of 1 in 14 and 1 in 22 respectively. There seems no reason why similar instability should not give rise to roll-waves when the bottom of the conduit is not plane, but has a curved section, so long as the section is uniform. If, however, the bottom is irregular, waves produced in this way will be deflected transversely and have their velocities changed at irregular intervals by the projections on the bed; hence they will only add to the general appearance of turbulence at the surface, without producing any characteristic roll-wave. It is presumably for this reason that regular roll-waves are not in general observable in mountain torrents.

I attempted to investigate the properties of travelling waves in the trough, but no definite results were obtained. It was clear that their velocity was distinctly greater than that of the water. They were timed over a measured distance to determine the velocity, but the results were not sufficiently accurate to give a definite test of any theory. They were consistent with the velocity of the waves relative to the water being either half the velocity of the water or the velocity of waves in standing water of the same depth; it proved impossible to discriminate between these two values. In the trough, of course, the waves did not grow to their full magnitude; their amplitude probably never exceeded a millimetre (and if it had done so, the determinations of the coefficient of skin friction made in this paper would have been vitiated). This fact is to be attributed to the shortness of the trough. Cornish remarks that in the Grünnbach the roll-waves were not completely formed when the water had been travelling along the conduit for 465 feet, the mean depth being about 3 inches. Thus for a mean depth of 5 mm. the water would have to travel 30 feet, about three times the length of my trough, before even this stage of development was reached.

SUMMARY.

Observations have been made of the flow of water in an inclined trough of rectangular section, with a planed wood bottom. Defining the Reynolds criterion for such a system as Q/ν, where Q is the total volume flux of water per unit breadth per unit time, and ν is the kinematic viscosity, it is found that turbulence first develops when the Reynolds number is about 310, distinctly less than the corresponding number for a pipe. When the Reynolds number is between 2 and 13 times the critical value, the observations are consistent with the skin friction coefficient κ being $0{\cdot}00253 \pm 0{\cdot}00006$, where the frictional force per unit area of the bottom is supposed to be $\kappa\rho u_1^2$, u_1 being the surface velocity. The mean velocity is about 0·94 of the surface velocity. The existence of a layer of water in laminar motion at the bottom of the trough was verified even at the highest velocities tested. The above interpretations have been put on the experimental results on the supposition that a uniform eddy viscosity exists at all depths between the free surface and the non-turbulent layer; on the same hypothesis it appears that the eddy viscosity must be equal to 0·0080 Q.

A theory has been constructed to account for certain travelling waves observed by Vaughan Cornish in steeply-inclined conduits. It appears that the uniform turbulent flow of a stream, with a plane free surface, becomes unstable when the mean slope exceeds 1 in 100, and that it is then replaced by a series of bores travelling faster than the water. Observational evidence is qualitatively consistent with the theory, but quantitatively several points remain to be tested.

LXXXV. *Wind-Channels in Aerodynamics.*

By N. K. Bose, *Ph.D.* (*Göttingen*), *Reader in Mathematics, Aligarh Moslem University, India**.

FOR experiments on aeroplanes and its parts, to determine the air resistances of tails and struts, the head and the fuselage, to calculate the lift and the drag, the angle of attack of wings, wind-channels have come to occupy a unique position. In fact, they offer the safest and, under certain circumstances, the most accurate method for determining the aerodynamical characteristics of an aeroplane. The only other accurate and reliable method is that in which aeronauts test their planes as to their reliability, controllability, and stability while they are in actual flight. This method, in so far as it affords a first-hand information, is of the utmost importance, but the amount of risk involved of danger to life and person prohibits its indiscriminate use. To minimize these difficulties and danger, to declare a plane safe for all practical purposes, experiments in wind-channels are now the only means at our disposal. Of course, the usefulness of wind-channels is limited by considerations of scale-effect in models and turbulences in air. Of recent years, Prandtl and Eiffel have shown that, if we could arrange the dimensions and velocities of the model experiments and of actual flights so that in both the cases Reynolds' number remains constant, scale-effect can be eliminated. This important discovery has extended the utility of wind-channel experiment to all those cases that are of any importance in aeronautics.

In wind-channel experiments, as is well known, the body to be experimented upon is placed in the channel through which a steady current of air is blown or drawn. By various means this current of air is rendered free from eddies, and the six components of forces on the body are measured. The quantities that concern wing-measurement most are its lift and drag for different angles of attack and the corresponding positions of the centre of wind-pressure, but these quantities measured in the channel are quite different from the corresponding quantities when measured in free space. We know that the stream-line generated by a body which is moving in a medium or over which the medium is passing whose boundaries extend to infinity, would be quite distinct from those in a limited medium. This fact of hydrodynamics will have to be taken into account in assigning any particular angle of attack to lift and drag coefficients, Ca, Cw. In any wind-channel experiment with wings, what is usually done is that the wing is set at a particular angle of attack (that is, the angle between the chord of the wing and the direction of the wind, which is usually horizontal, measured) and its corresponding lift and drag are then experimentally determined. But this geometrically measured angle of attack, it will be seen, is not the same as the real or effective angle of attack. By effective angle of attack is meant that angle which the real stream-lines make wlth the chord of the wing.

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* Communicated by the Author.

At first, let us consider the case of a plane or a wing of limited dimensions placed in a medium of unlimited extent flowing steadily in a direction, say, horizontal. This will call forth a vertically downward disturbance in the medium (disturbances in other directions we are not at present concerned with) which is mechanically known as downwash. This downwash of a wing, as is apparent, will modify its own lift capacity—*i. e.*, its angle of attack will be diminished by the amount $\tan^{-1}\frac{w_0}{V}$, where w_0 is the downwash velocity on the wing and V the velocity of the free stream at infinity. We know that the lift and the angle of attack of a wing are connected by the following simple relation when the angle of attack is small :

$$A = \mathrm{CaFq} \quad \text{and} \quad \mathrm{Ca} = 2\pi(\alpha_\infty + \beta),$$

where A is the lift and Ca the lift-coefficient, F the area of the wing, $q = \frac{1}{2}\rho V^2$, α_∞ is the angle of attack of a wing of infinite lateral extents, and β is the angle which the sectional arc of the wing subtends at its centre (when the radius of curvature of the wing is very great). It has been found by experiment that Ca and α are linearly connected, and theory gives for wings of circular section

$$\mathrm{Ca} = 2\pi(\alpha_\infty + \beta)$$

per unit breadth, and

$$\sin \beta/2 = t/R_1,$$

where $2t$ is the sectional chord and R_1 the radius of the earth. Now this angle of attack α_∞, which is called the angle of attack for a wing of unlimited length, cannot be found directly from experiment, as when the plane is of unlimited length the downwash is absent, so that the angle between the chord of the aeroplane section and the direction of flow of air current gives the angle of attack; but when we have to deal with a finite length of the plane, this downwash comes in, so that what is the real direction of the current at infinity is no longer the real direction in which the air current strikes the chord of the plane, and the geometrical angle of attack is consequently not the real or effective angle of attack of the aeroplane. So in the case of a monoplane, when we have got to calculate the lift from the geometrical angle of attack we have to transform the geometrical angle which is measured from experiment to the effective angle of attack at which the wind really strikes the chord. This formula for transformation for a monoplane is

$$\alpha_\infty = \alpha - \tan^{-1}\frac{w_0}{V},$$

as we can easily see that the downwash gives the free stream velocity V a downward component, w_0, and the resultant goes at an angle $\tan^{-1}\frac{w_0}{V}$ to the direction of V, so that the geometrical angle of attack is diminished by this amount.

So far we have not considered the influence of the channel. This influence of the channel, it will be broadly seen, will be to introduce a further modification in the angle of attack. The disturbances due to the channel will consist in superimposing another downwash, called induced downwash w_0', and in giving a curvature to the stream-lines given by

$$\frac{1}{R} = \frac{\partial}{\partial y}.\tan^{-1}\frac{w_0'}{V} = \frac{1}{V}\frac{\partial w_0'}{\partial y} = \frac{1}{V}\left(\frac{\partial w'}{\partial y}\right)_0,$$

if w_0' is small in comparison with V, where y is measured along the stream and the curvature is taken in a vertical plane of a stream-line as it crosses the vertical plane of the wind.

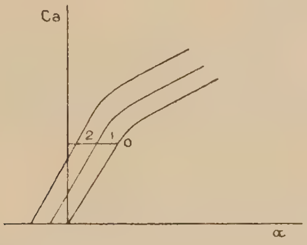
The effect of this induced downwash is apparent, and the change in the angle of attack will be $\tan^{-1}\frac{w_0'}{V}$. Hence, when only the two downwashes are considered

$$\alpha_\infty = \alpha - \tan^{-1}\frac{w_0}{V} - \tan^{-1}\frac{w_0'}{V}.$$

The effect of the induced curvature will be somewhat complicated and must be considered in detail.

Suppose we have three planes, 0, 1, 2, of which 0 has got no curvature, 1 has a curvature $1/R_1$, and 2, $1/R_2$. It has been found from experiment that the relation between Ca, the lift-coefficient, and α, the angle of attack, is given by the accompanying figure for 0, 1, 2. Then it is apparent that 2 has a smaller angle of attack than 1, and 1 smaller than 0 for the same lift-coefficient Ca. This fact can be

Fig. 1.



theoretically expressed by the relation

$$A = 2\pi \rho t V^2 \sin(\alpha + \beta/4),$$

where ρ is the density of the medium. If f be the height of the middle point of the arc above the chord,

$$\frac{f}{t} = \tan \beta/4 \quad \text{and} \quad R_1 = \frac{f^2 + t^2}{2f},$$

$$\text{or} \quad 1/R_1 = 2f/(t^2 + f^2),$$

$$t/R_1 = 2f/t = \beta/2.$$

$$\therefore \quad Ca = 2\pi \sin(\alpha + \beta/4)/\cos \beta/4$$

$$= 2\pi(\alpha + \beta/4) = 2\pi(\alpha + t/2R_1).$$

From this it is apparent that, if we want to have the same lift-coefficient, Ca, for the three planes, the angle of attack must be diminished by amounts $t/2R_1$ for 1 and $t/2R_2$ for 2, where t is half the breadth of the plane and $1/R$ is the curvature of the surface of the plane.

Thus, when the stream-lines are straight the effect of the curvature of the plane is to diminish the angle of attack for the same lift-coefficient by $t/2R$.

If now we want to find the effect of a curvature in the stream-lines on a plane which has got also curvature of its own, then if $1/R$ be the curvature of the stream-lines and $1/R_1$ that of the plane, the effective curvature of the plane in this case is only $1/R_1 - 1/R$. By effective curvature we mean the curvature of the plane which is effective in bringing about a diminution of the angle of attack. So in this case when a curved plane finds itself in a stream whose stream-lines have got a curvature of their own, to have the same lift-coefficient Ca as it had when the stream was straight, the angle of attack must be diminished by $\frac{t}{2}\left(\frac{1}{R_1}-\frac{1}{R}\right)$. So the geometrical angle of attack must be diminished by

$$\frac{t}{2R_1}-\frac{t}{2}\left(\frac{1}{R_1}-\frac{1}{R}\right)=\frac{t}{2R}.$$

Hence the effective angle of attack of a wing in a wind-channel whose geometrical angle of attack is measured is given by

$$\alpha_\infty=\alpha-\tan^{-1}\frac{w_0}{V}-\tan^{-1}\frac{w_0'}{V}-\frac{t}{2R}.$$

Generally w_0 and w_0' are comparatively small in comparison with V. Hence

$$\alpha_\infty=\alpha-\frac{w_0}{V}-\frac{w_0'}{V}-\frac{t}{2R}.$$

Thus the problem of a wind-channel resolves itself into finding w_0, w_0', and $1/R$, *i.e.*, the two downwashes and curvature of the stream-lines. For our present purpose we want all these quantities on the wing itself.

To find the influence of a wing on the surrounding medium reference must be made to a former paper of mine in this Magazine (*vide* Phil. Mag. xlviii. p 113, July 1924). There the aeroplane surface or wing surface has been divided into so many differential surfaces, so that each small elemental surface may be looked upon as an aeroplane on which fluid pressure is calculated independently of all other elements, and then it is integrated throughout the whole volume occupied by these elemental aeroplanes. The conception is something like this; at each elemental aeroplane there is a circulation which is denoted by γ, and from the edges of this element vortices flow off with the fluid; the strength of the elemental vortices is ϵ. So we can picture a thing like this: under each differential aeroplane there is a vortex of strength γ which is fixed with the element, and from each element a vortex line is flowing off with the liquid whose strength per unit volume is ϵ, so that the aeroplane becomes the seat of innumerable fixed vortices of strength γ per unit volume, and from the aeroplane free vortices are flowing off with the liquid like ribbons with strength ϵ per unit volume.

Again it has been observed experimentally that the density of the lift of a wing (lift per unit length) is not constant over the whole length of the wing, but in general falls off gradually from a maximum at the middle to 0 at the ends. In accordance with what has been proved there corresponds to this a circulation decreasing from within outwards. Therefore, according to the theorem that by the displacement of a closed curve round the wing the circulation Γ can only change if a corresponding quantity of vortex filament proceed off from the trailing edge, wherever Γ changes a vortex filament will flow off with the liquid, and as Γ changes from point to point of the wing these filaments flow off from every point of the wing. Here a special arrangement of the vortex filament will help us in our mathematical treatment. We suppose that a vortex filament of strength $\Gamma(x)$, with a right-handed screw rotation, coming from infinity behind the plane meets the lifting line (the single line vortex which replaces all the bound vortices and passes through the C. G. of the vortices) at a distance x from the middle of the wing measured to the right of the pilot. This filament then turns towards the right forming a part of the lifting line, goes a short distance dx along it, and then again turning to the right goes to infinity parallel to the incoming filament. Then another filament of strength $\Gamma+d\Gamma$ travelling from infinity in the same plane as the former filament pair meets the lifting line at $x+dx$ and behaves as the former one did. Thus we see that at every point of the lifting line a filament of strength Γ goes out and one of strength $\Gamma+d\Gamma$ comes in, so that at every point of the lifting line a vortex filament of strength $d\Gamma$ will be coming in and the lifting line will be a vortex line of strength $\int d\Gamma=\Gamma$. With this arrangement of the vortices we are now in a position to remove the wing and consider its effect on the surrounding medium by replacing it by this vortex arrangement.

The law according to which the lift or the circulation Γ varies with x, *i.e.* with the distance from the middle of the plane, is fairly well known. It is evident that it depends on the aspect-ratio and the perspective of the plane. A remarkable distribution of circulation was found in the form

$$\Gamma=\Gamma_0\sqrt{1-\frac{x^2}{l^2}},$$

where Γ_0 is the circulation at the middle and l the half-span of the wing. This distribution is called Elliptic Distribution of Lift, and has a peculiar property of giving to a monoplane the smallest drag that is possible for it with the total lift, the span, and the velocity given. Another characteristic in its favour is that all distributions that have as yet been observed deviate but slightly from this, so that any conclusion drawn from the assumption of elliptic distribution will not go very wide of the mark. Another outstanding feature of this distribution is that it gives a constant downwash velocity over the whole span of the wing; it is given by

$$w_0 = \frac{\Gamma_0}{4l},$$

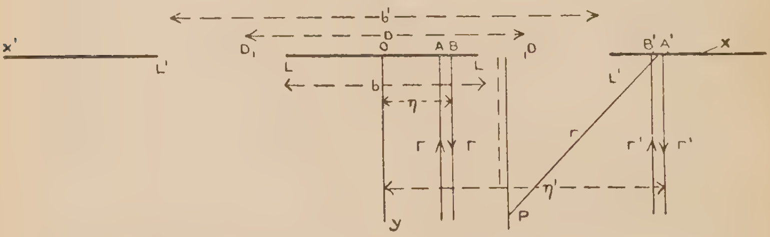
and for this distribution

$$A = \tfrac{1}{2}\pi\rho V l \,.\, \Gamma_0,$$

$$\therefore \quad w_0 = \frac{A}{2\pi\rho V l^2}.$$

When this vortex system is placed in a medium which is bounded by the walls of a wind-channel, we know that the boundary (which is assumed circular here) may be removed and its effect calculated by replacing it by the images of the vortices at the inverse points. The accompanying figure will make it clear.

Fig. 2.



The above figure is in the plane of the vortices which is horizontal, LOL is the wing, O its middle point, D and D are the points of section with the canal, L′ is the inverse point to L with respect to the circle, the inverse vortices extend to infinity along L′X and L′X′, OY is horizontal and taken along the direction of the stream. One vortex Γ enters LOL at A $(x, 0)$ and goes out at $(x+dx, 0)$, the inverse point B also possesses a vortex Γ′ coming in and at A′ going out. We have

$$\Gamma = \Gamma_0 \surd(1-4\eta^2/b)$$

$$\Gamma' = \Gamma_0 \surd(1-4\eta^2/b^2) = \Gamma_0 \surd(1-b'^2/4\eta'^2),$$

where

$$b=2l, \quad b'=\mathrm{L'OL'}.$$

w_1 = vertical component of the velocity induced by the vortex at B′ at P (x, y)

$$= -\frac{\Gamma'}{4\pi(\eta'-x)}\left(1+\frac{y}{r}\right).$$

The pair of vortices at B′ and A′ having the same strength Γ′ but different rotation, produces then a vertical velocity at P which can be written as the difference of the effects of the two vortices at A′ and B′ which are closed together :

$$dw_1 = \frac{\partial w_1}{\partial \eta'} d\eta' = \frac{\Gamma'}{4\pi}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right) + \frac{1}{\eta'-x}\cdot\frac{y}{r^2}\cdot\frac{\partial r}{\partial \eta'}\right] d\eta'$$

$$= \frac{\Gamma'}{4\pi}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right) + \frac{y}{r^3}\right] d\eta'.$$

Due to the cross-vortex B′A′,

$$dw_2 = \frac{\Gamma' d\eta'}{4\pi}\cdot\frac{y}{r^3}.$$

Hence the whole downward induced velocity at P due to the bound and the free vortices at B′ and A′

$$dw' = \frac{\Gamma' d\eta'}{4\pi}\left[\frac{1}{(\eta'-x^2)}\left(1+\frac{y}{r}\right) + \frac{2y}{r^3}\right] d\eta'.$$

$$\therefore \quad w' = \frac{\Gamma_0}{4\pi}\int_{b'/2}^{-b'/2}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right) + \frac{2y}{r^3}\right]\sqrt{\left(1-\frac{b'^2}{4\eta'^2}\right)} d\eta',$$

$$w_0' = \frac{\Gamma_0}{4\pi}\int_{b'/2}^{-b'/2}\frac{\sqrt{1-b'^2/4\eta'^2}}{(\eta'-x)^2} d\eta',$$

since $y = 0$ on the wing where w_0' is taken.

Putting

$$\xi = \frac{2b}{D^2}\cdot x = \frac{2x}{b'}, \quad \text{and} \quad \frac{b'}{2}X = \eta', \quad \therefore \quad X > 1.$$

Hence

$$w_0' = \frac{\Gamma_0}{4\pi}\int_1^{-1}\frac{\sqrt{1-\frac{1}{X^2}}}{\left(\frac{b'^2}{2}X - x\right)^2}\cdot\frac{b'}{2} dX$$

$$= \frac{\Gamma_0}{2\pi b'}\int_1^{-1}\frac{\sqrt{X^2-1}}{X(X-\xi)^2} dX$$

$$= \frac{A}{\pi D^2 \rho V}\left(1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4 + \frac{35}{128}\xi^6 + \ldots.\right).$$

Again

$$\left(\frac{dw'}{dy}\right)_{y=0} = \frac{3\Gamma_0}{\pi b'}\int_1^{-1} \frac{\sqrt{X^2-1}}{X(X-\xi)^3}\,dX$$

$$= 3\frac{dw_0'}{d\xi}$$

$$= \frac{3A}{\pi D^2\rho V}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3 + \frac{105}{64}\xi^5 + \ldots\ldots\right).$$

We have put

$$\xi = \frac{2b}{D^2}x = \frac{4l}{4R^2}x = \frac{l}{R}\cdot\frac{x}{R},$$

where R is the radius of the channel. In ordinary experiment $\frac{l}{R}$ does not extend beyond 1/2 and $\frac{x}{R}$, as the point must be on the wing itself, cannot be greater than half. Hence, generally $\xi < \frac{1}{4}$ and in w_0' we need not take more than three terms, and in $\left(\frac{dw'}{dy}\right)_0$ more than two. Thus ultimately, we have

$$w_0 = \frac{A}{2\pi\rho l^2 V}$$

$$w_0' = \frac{A}{\pi\rho D^2 V}\left(1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4 + \ldots\ldots\right),$$

and

$$\frac{1}{R} = \frac{1}{V}\left(\frac{\partial w'}{\partial y}\right)_0 = \frac{3A}{\pi\rho D^2 V^2}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3 + \ldots\ldots\right).$$

With these, the effective angle of attack α_∞ of a wing in a wind-channel experiment with a measured angle of attack,

$$\alpha_\infty = \alpha - \frac{A}{2\pi\rho l^2 V^2} - \frac{A}{\pi\rho D^2 V^2}\left(1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4\right)$$
$$- \frac{3At}{2\pi\rho D^2 V^2}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3\right),$$

where $\xi = \frac{l}{r}\cdot\frac{x}{R}$ and A, α are found experimentally.

The importance of this formula will be at once apparent, if we remember that in all wind-channel experiments it is the angle of attack which distinguishes one set of experiments from others. In the above I have not considered the influence of the breadth of the wing, as I have replaced the wing by a line vortex only. The peculiar distribution of vortices over the breadth of the wing that will satisfactorily replace it has been discussed by Dr. Birnbaum in his paper in the *Zeitschrift für angewandte Mathematik und Mechanik*, 1924. In my dissertation ("Das Doppledeckerproblem," Göttingen, 1923) I have discussed this effect in the case of a biplane, and a corresponding treatment might be done in this case. I must wait till some experimenters see how the above formula works.

In practice the average value of α_∞ over the whole span of the wing must be taken.

In the above, I have considered the case of a wind-channel in which the whole experiment is conducted in a closed place. Eiffel's method consists in experimenting in a blast of air drawn through a room, whose dimensions are large in comparison with the radius of the column of air-blast. Prandtl's improved method consists in placing a gap between two wind-channels. A current of air is drawn through the walls of a wind-channel, and then through a gap it is drawn into another wind-channel. This method combining the former two eliminates their defects. In both Prandtl's and Eiffel's methods $\Gamma' = -\Gamma$.

LXXXVI. *Longitudinal Asymmetry in the Direction of Ejection of Photo-electrons.* By Ona K. de Foe, *Teaching Fellow in Physics, Washington University, Saint Louis, Missouri* *.

Introduction.

WHEN radiation falls normally upon a thin plate and ejects photo-electrons, it is observed that the number of photo-electrons proceeding from that side of the plate from which the radiation emerges (emergent side), exceeds the number of photo-electrons from that side upon which the radiation is incident (incident side). This effect appears to have been discovered by Eve[1] while attempting to show the similar natures of gamma and X-rays. Eve observed that the ionization current from the emergence side of a thin plate bombarded normally by gamma rays was not so much less than the ionization current from the incident side as the absorption of gamma rays indicated it should be for the thickness of metal used.

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* Communicated by Prof. F. W. Bubb.

[1] Eve, Phil. Mag. viii. p. 669 (1904).

In the region of gamma rays this effect has been examined by Wigger[2], Dawes[3], Mackenzie[4], and Bragg and Madsen[5]. In the region of ultra-violet light this phenomenon has been studied experimentally by Stuhlmann[6], Kleeman[7], Robinson[8], and Piersol[9]. Experiments in the X-ray region have been carried out by Beatty[10], Cooksey[11], Wilson[12], and Bubb[13].

There are two possible explanations of this effect. We may suppose, in the first place, that the velocity of the photo-electrons from the emergence side exceeds the velocity of those from the incidence side and that the number of photo-electrons from the two sides are equal. We may, on the other hand, suppose that the velocities from the two sides are equal and that the numbers are unequal.

The experimental work of Beatty[10] with X-rays and the work of Piersol[9] with ultra-violet light on this question, seem to decide in favour of the second alternative. For these observers find that the retarding potentials (and consequently the velocities) for the two sides of the plate are equal. Further light is furnished by the photographs of Wilson[12], Bubb[13], and those of the present experiment, of the tracks of photo-electrons. These photographs show definitely that the number of emergence (or forward) exceeds the number of backward photo-electrons. Furthermore, these photographs show the average range to be independent of direction.

On the theoretical side the evidence is also in favour of the supposition that the effect is due solely to the excess number of forward photo-electrons. Millikan[14] points out that, if the velocity of ejection depends on direction of ejection, Einstein's photo-electron equation

$$h(\nu-\nu_0) = mc^2(1/\sqrt{1-\beta^2}-1)$$

does not hold. For, in order to make it apply, we should have to assume that h also depends on the direction of ejection. However, h is found experimentally to be independent of the direction of ejection of the photo-electron.

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[2] Wigger, *Phys. Zeitschr.* p. 683, Oct. 26, 1905.

[3] Dawes, Phys. Rev. xx. p. 182 (1905).

[4] Mackenzie, Phil. Mag. xiv. p. 176 (1907).

[5] Bragg and Madsen, Phil. Mag. xv. p. 613 (1908).

[6] Stuhlmann, Phil. Mag. xxii. p. 854 (1911).

[7] Kleeman, 'Nature,' May 19, 1910.

[8] Robinson, Phil. Mag. xxv. p. 115 (1913).

[9] Piersol, Phys. Rev. xxiii. p. 144 (1924).

[10] Beatty, Proc. Camb. Phil. Soc. xv. p. 25.

[11] Cooksey, Phil. Mag. xxiv. p. 37 (1912).

[12] Wilson, Proc. Roy. Soc. lxxxvii. p. 277 (1912); civ. p. 1 and cv. p. 22 (1923).

[13] Bubb, Phys. Rev. xxiii. p. 137 (1924).

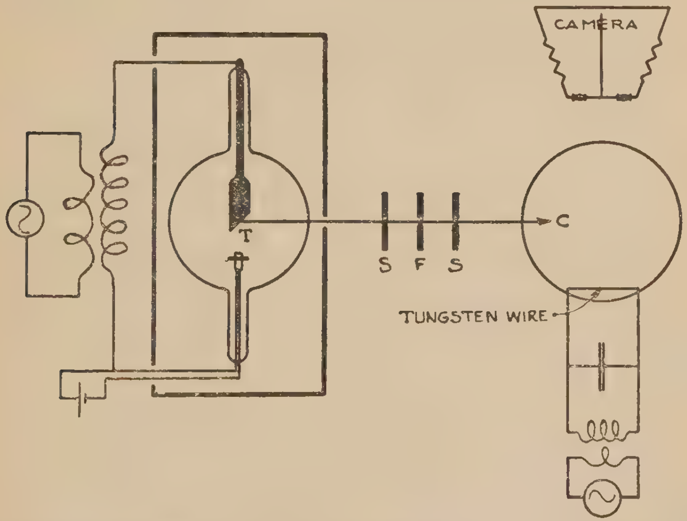
[14] Millikan, Phys. Rev. vii. p. 18 (1916).

There is a somewhat surprising lack, however, of definite experimental information as to the effect, on the ratio of forward to backward photo-electric current, of such obviously essential matters as the frequency of the radiation and the source of the photo-electrons. With the sole exception perhaps of Cooksey's work, all previous work possesses little more than qualitative value.

The present experiment was performed for the purpose of obtaining a definite value of the ratio of the forward to the backward photo-electric current excited in a given substance by radiation of a definite frequency.

Experimental Procedure.

In this experiment the photo-electrons were ejected from air by the K_α radiation from molybdenum. The directions of ejection of the photo-electrons were determined by taking stereoscopic pictures, by the Wilson cloud method, of the ionization tracks of the photo-electrons. The number of forward and backward tracks were counted and their ratio determined



Experimental arrangement for photographing photo-electron tracks.

The apparatus was arranged as illustrated in the figure.

A beam of X-rays TC from the molybdenum target of a Coolidge tube driven at 30 k.v. and about 20 m.a. was directed through the lead slits SS and a zirconium phosphate filter F into the expansion chamber C of a Wilson cloud expansion apparatus. The purpose of the slits was to limit the beam and hence afford a control of the number of tracks. Too many tracks destroy the value of a photograph, since one is unable visually to untangle the tracks and clearly distinguish which end is the origin of the track. Zirconium was used as a filter since it is particularly transparent to the K_α line of molybdenum, while highly absorbent of the K_β and K_γ lines and of the white radiation.

On the under side of the plate-glass top of the expansion chamber was a thin film of gelatin made conducting by a small amount of boric acid. On the top of the piston forming the bottom of the chamber was a similar conducting layer of gelatin made black by india ink. A difference of potential of about 60 volts per cm. was maintained across the expansion chamber until just before the expansion.

In taking the photographs a very intense instantaneous illumination is necessary. Some preliminary experiments showed that tungsten filaments exploded by the discharge of a high-tension condenser furnish a satisfactory illumination. A single three mil tungsten filament 10 cm. long placed at the focus of a semicylindrical mirror was found sufficient. The condenser which furnished the current to explode the filament was charged by a small 30 k.v. transformer with thermionic valve in circuit. The light was directed into the expansion chamber through a slit in a black paper covering the top of the chamber. The chamber and camera were, of course, protected by suitable screens.

The photographs were taken with a stereoscopic camera. The matched lenses were marked 5·5 focus f. 4·5. The distance between lenses was 7·3 cm., and they were operated at full aperture. The photographic plate was placed vertical and parallel to the beam. This was considered to be the best position of the plate for examining the forward and backward tracks. Graflex Seed 60 plates were found satisfactory.

The timing of the various events was managed by a heavy pendulum having suitable devices placed in its path. After the room had been darkened and the camera opened the pendulum was released. This caused the following events to occur:—A weight was released which pulled the cork separating the under side of the piston from a vacuum chamber, thus causing the expansion. The electric field across the chamber was removed and the top and bottom gelatin plates were short circuited. (It was found necessary to do this, as otherwise they acted as a condenser and maintained the electric field across the chamber for a sufficient time to affect the shape of the tracks.) The X-rays were started by closing a switch in the primary of the transformer driving the X-ray tube. The tungsten filament was exploded thus illuminating the tracks for the photograph. The timing of these events was adjusted by trial to give a satisfactory picture.

Experimental Results.

About 50 stereoscopic pictures of the tracks of photo-electrons ejected from air by the homogeneous K_α radiation from molybdenum were obtained. The following general observations may be made:—The number of tracks whose initial directions had a forward component greatly exceeds the number of tracks which started with a backward component. About 30 per cent. of the tracks counted started nearly at right angles to the beam of X-rays. Not more than 1 per cent. of the tracks started either exactly forward or exactly backward. Most of the tracks started within 45° of the plane normal to the beam of X-rays.

Three distinct types of tracks could be clearly distinguished: (1) a set of tracks having no appreciable length, (2) a set averaging about ·5 cm. in length, and (3) a set averaging about ·9 cm. in length. The first set is the type C. T. R. Wilson calls sphere tracks. He attributes them to the K radiation of argon ejecting from oxygen or nitrogen, the argon having been put into a state to radiate by having lost one of its K electrons through ejection by the primary radiation. The second set is probably due to the photo-electrons ejected from the argon K ring by the primary X-rays. The third and longest set may be attributed to the photo-electrons ejected from oxygen and nitrogen K rings by the primary X-rays.

A count was made of tracks which started with a forward component along the beam and also a count of those which started with a backward component. In each case only those tracks were counted both of whose ends could be clearly distinguished and where no doubt existed as to which end was the origin of the track. The result of this was that a larger proportion of the short argon tracks were counted, since they are shorter and consequently more easily distinguished among a tangled set of tracks. By count it appears that about 59 per cent. of the tracks counted were due to photo-electrons ejected from the argon K ring, while about 41 per cent. were from oxygen and nitrogen K rings.

These latter could not be distinguished from each other as their difference in length of track was too small. The results obtained by one observer were 188 forward tracks and 69 backward tracks, giving a ratio of 2·74. A second observer found 206 forward and 68 backward tracks, giving a ratio of 3·03. The average ratio of forward to backward tracks is then 2·89.

Discussion.

Rutherford states[15] that the results obtained by previous observers using plates as source of photo-electrons are not inconsistent with the view that all the photo-electrons proceed initially exactly forward with the radiation. The photographs obtained by Wilson[12], by Bubb[13], and those obtained in this experiment show, however, that a large number of the tracks plainly start with a component backward. This seems to decide definitely against Rutherford's view.

Richardson has proposed[16] the view that the radiation pressure in the forward direction is the cause of the excess number of forward photo-electrons. He points out that the momentum of the quantum in the forward direction as given by the electromagnetic theory is $mv = h\nu/c$. We might suppose that this momentum, as well as the energy of the quantum, is given to the photo-electron.

A quantum theory of this effect based on the following hypothesis has been proposed by Bubb[17]: "A quantum of radiant energy which ejects a photo-electron from an atom imparts its energy $h\nu$ to the atom by means of an impulse which has the constant forward component $h\nu/c$ and a sideways component in the direction of the electric vector of the radiation." The orbital electron just previous to its conversion into a photo-electron is assumed to have its momentum in a random direction given in magnitude by the Bohr theory. On this basis the ratio of the forward to the backward photo-electrons is calculated to be

$$R = \{\lambda\sqrt{82{\cdot}44\lambda_0 - 1} + \lambda_0 - {\cdot}0242\}/\{\lambda\sqrt{82{\cdot}44\lambda_0 - 1} - \lambda_0 + {\cdot}0242\},$$

where λ is the wave-length in Å. of the homogeneous radiation causing ejection and λ_0 is the critical ionization wave-length in Å. of the element from which the photo-electron is ejected.

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[15] Rutherford, 'Radioactive Substances and their Radiations,' p. 275.

[16] Richardson, Phil. Mag. xxv. p. 144 (1913).

[17] See present number of Phil. Mag. p. 824.

To apply this formula we have the following data:—The average wave-length of the K_α doublet of molybdenum is $\lambda = \cdot 71$ Å. The critical ionization wave-lengths of the principal constituents of the air are: argon $\lambda_0 = 3\cdot 87$, oxygen $\lambda_0 = 23\cdot 9$, and nitrogen $\lambda_0 = 31\cdot 0$. The formula gives the corresponding values of R as follows: argon $R = 1\cdot 88$, oxygen $R = 7\cdot 32$, and nitrogen $R = 13\cdot 2$. It may be seen that the experimental value 2·89 is larger than the value for argon and less than the values for oxygen and nitrogen and is of the proper order of magnitude.

On the basis of the absorption formula $\lambda^3 Z^4 N$ (where λ is the wave-length of the radiation producing ejection, Z is the atomic number of the source of the photo-electron, and N is the number of atoms present) C. T. R. Wilson has calculated that 15 per cent. of the tracks in air should be from argon, 25 per cent. from oxygen, and 60 per cent. from nitrogen. It is certain, however, by actual observation of length of track, that in the present experiment about 59 per cent. of the tracks counted were from argon, and the remaining 41 per cent. from oxygen and nitrogen. As explained above, this is due to the fact that the short argon track can be more easily untangled visually from a large number or group of interlacing tracks than can the longer tracks from oxygen and nitrogen. On the basis of Wilson's figures the 41 per cent. may be divided into two classes, 13 per cent. from oxygen and 28 per cent. from nitrogen. The composite ratio[18] should then be theoretically,

$$R = (1\cdot 88 \times \cdot 59/2\cdot 88 + 7\cdot 32 \times \cdot 13/8\cdot 32 + 13\cdot 2 \times \cdot 28/14\cdot 2)/(\cdot 59/2\cdot 88 + \cdot 13/8\cdot 32 + \cdot 28/14\cdot 2) = 3\cdot 38.$$

The experimental ratio 2·89 agrees within 15 per cent. of the theoretical value. In view of the comparatively small number of tracks and the fact that the air is a mixture of so many gases, this agreement is good confirmation of the theory upon which the formula was based.

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[18] It was at first considered possible from an experiment on air to find separate ratios for all three gases, argon, oxygen, and nitrogen. Although it is generally possible to distinguish between an argon track and a track from oxygen or nitrogen, even this cannot always be done, while it is altogether impossible to distinguish between a track from oxygen and one from nitrogen. In view of this a composite or average ratio is given for the mixture rather than the very uncertain separate ratios for the individual gases.

It is proposed to continue these researches by repeating the experiment with only pure gases in the expansion chamber.

I wish to thank Professor F. W. Bubb for advice and assistance in performing this experiment and for criticism of the manuscript.

LXXXVII. *A Quantum Theory on the Asymmetries in the Direction of Ejection of Photo-electrons.* By Frank W. Bubb, *National Research Fellow, University of Chicago**.

INTRODUCTION.

TWO types of asymmetry in the direction of ejection of photo-electrons produced by high-frequency radiation have been noted. These two asymmetries may be distinguished by the term "longitudinal" and "lateral."

Longitudinal Asymmetry.—Mackensie[1] first showed that unequal photo-electric currents are obtained from the two sides of a thin plate bombarded normally by gamma rays. A larger current is obtained from that side of the plate from which the gamma rays emerge than from that side upon which the gamma rays are incident. Experiments in which the ratio of the emergent to the incident photo-electric current was measured have been performed by Bragg[2] with gamma rays, by Stuhlmann[3] and Kleeman[4] with ultra-violet light, and by Cooksey[5] and Beatty[6] with homogeneous X-rays. The results of these experiments indicate that the asymmetry increases with the hardness of the radiation, the ratio of emergent to incident current increasing from 1·17 for ultra-violet light upon platinum films to as high as 20 for gamma rays traversing carbon plates.

C. T. R. Wilson[7] and the writer[8] have presented visual evidence of this effect in cloud-expansion photographs of the tracks of photo-electrons. In discussing his photographs, Wilson notes that a majority of the tracks have a forward component comparable with the lateral component. The writer, from an examination of his own photographs, obtains the result that 17 per cent. of the tracks have an initial backwards component, 32 per cent. are ejected almost exactly at right angles to the beam of X-rays, and 51 per cent. have an initial forward component.

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* Communicated by the Author.

[1] Mackensie, Phil. Mag. xiv. p. 176 (1907).

[2] W. H. Bragg, Phil. Mag. xv. p. 663 (1908).

[3] Stuhlmann, Phil. Mag. xxii. p. 854 (1911).

[4] Kleeman, 'Nature,' May 19 (1910).

[5] Cooksey, Phil. Mag. xxix. p. 37 (1912).

[6] Beatty, Proc. Camb. Phil. Soc. xv. 6, p. 492 (1910).

[7] C. T. R. Wilson, Proc. Roy. Soc. civ. (1923).

[8] F. W. Bubb, Phys. Rev. ii. p. 137 (1924).

The work of Beatty [6] and Piersol [9] shows that this effect is due to the excess number of forward over backward photo-electrons, for both these observers find the same velocity for forward and backward photo-electrons. This result is further supported by the photographs of Wilson [7] and by those of the writer [8] which show that the forward and backward tracks have the same average range.

Lateral Asymmetry.—The writer has photographed by Wilson's cloud method the tracks of photo-electrons ejected from air by plane polarized X-rays. These photographs show [8] a strong concentration of photo-electrons ejected nearly parallel to the electric vector of the polarized radiation, and consequently in a single direction perpendicular to the beam. This effect has also been observed by Wilson [7]. As a consequence of this lateral asymmetry, one should expect most of the photo-electrons ejected by unpolarized radiation to be at random in directions nearly normal to the beam. In this case, however, there should be no asymmetry with respect to any particular line normal to the beam as in the case with polarized beams. The effect with unpolarized beams has been previously noted by A. H. Compton [10].

Quantum Impulse Hypothesis.

These two types of asymmetry suggest the following hypothesis, which, it may be shown, is sufficient to account for a number of the photo-electric phenomena. A quantum of radiant energy which ejects a photo-electron from an atom imparts its energy $h\nu$ to the atom by means of an impulse which has the constant forward component $h\nu/c$ and a sideways component in the direction of the electric vector of the radiation.

This hypothesis really consists of three parts. In the first place, it assumes that the whole energy quantum $h\nu$ is given to the atom[11]. This view will, of course, meet with general acceptance; for the work of Millikan[12] on Einstein's photo-electric equation definitely identified the constant with Planck's constant h. The beautiful work of de Broglie[13] with X-rays and of Ellis[14] with gamma-rays, on the magnetic spectrum of photo-electrons, shows that Einstein's equation can be put in the form

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[9] Piersol, Phys. Rev. ii. p. 144 (1924).

[10] A. H. Compton, Bull. Nat. Res. Coun. no. 20, p. 25 (1922).

$$h(\nu-\nu_0)=mc^2(1/\sqrt{1-\beta^2}-1),$$

where ν_0 is the critical ionization frequency (the other quantities have their usual meaning) corresponding to the particular energy level from which the photo-electron is (assumed to be) ejected. In view of this, it is generally accepted that the photo-electron receives initially the whole energy quantum, and that its smaller kinetic energy on emerging is accounted for by the energy loss in escaping from the atom.

In the second place, the hypothesis assumes that the atom receives a forward impulse $h\nu/c$. In support of this view, it may be pointed out that both the classical electromagnetic theory and the relativity theory attribute momentum to energy in motion, and both agree in assigning the momentum $h\nu/c$ to the quantum $h\nu$ in motion with the velocity of light. A. H. Compton's work[15] on the change of wave-length due to the scattering process lends additional support to this view; for Compton treats, in effect at any rate, the quantum as though it were a corpuscle of forward momentum $h\nu/c$, which is scattered simply by bouncing off an electron. Surely on this view then, if the quantum delivers all its energy (itself, so to speak) to the atom, we may reasonably suppose all its forward momentum to be also delivered to the atom. This assumption has been used previously by O. W. Richardson[16] in an attempt to explain the Mackensie asymmetry.

Finally, we assume that a sideways impulse parallel to the electric vector of the radiation also acts on the photo-electron to eject it. The writer's work on the lateral asymmetry in the direction of ejection of photo-electrons produced by polarized X-rays is good experimental support for this view. Furthermore, it is to be expected on the classical electromagnetic theory that the electric force of the radiation is effective in ejecting the photo-electron.

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[11] The term atom will be used to denote the system before ejection of the photo-electron. The portion of the atom which remains after ejection of the photo-electron will be called the photo-atom. In this sense, then, the atom consists of two parts—the photo-electron and the photo-atom.

[12] Millikan, Phys. Rev. vii. p. 355 (1916).

[13] M. de Broglie, *Jour. de Phys. et Rad.* ii. p. 265 (1921).

[14] Ellis, Proc. Roy. Soc. xcix. p. 261 (1921).

[15] A. H. Compton, Phys. Rev. xxi. p. 284 (1923).

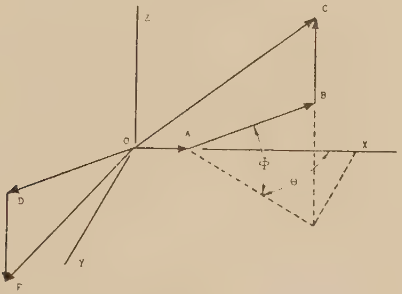
[16] Richardson, 'The Electron Theory of Matter,' p. 478.

This hypothesis has the virtue of supplying us with a momentum relation in addition to the Einstein photo-electric relation. We cannot expect the Einstein equation, concerned only with energy, to supply a complete dynamical basis for the explanation of the photo-electric effect.

Momentum and Energy Relations.

The principle of the conservation of momentum requires that the vector sum of the momentum of the system, which we shall suppose to consist only of the quantum, the photo-electron, and the photo-atom[11], shall be the same before and after separation.

Fig. 1.



The momentum relations involved in the ejection of a single photo-electron by a single quantum of radiation.

In fig. 1 let O be the position of an atom about to be disrupted by a quantum $h\nu$ proceeding in the direction OX and having its electric vector parallel to OZ (the radiation is then in the usual sense polarized in the XY plane). Before ejection of the photo-electron the momentum consists of three parts: the momentum

$$h\nu/c = \mathrm{OA}$$

of the quantum; the momentum

$$m\beta_0 c/\sqrt{1-\beta_0^2} = \mathrm{AB}$$

of the photo-electron in its atomic orbit, where m is its rest mass and β_0 the ratio of its velocity to c, the velocity of light; and the momentum OD of the photo-atom. If we assume that the momentum of the whole atom is negligible, the momentum OD of the photo-atom before separation is equal and opposite to that of the orbit-electron. After separation the momentum consists of two parts: the momentum

$$m\beta c/\sqrt{1-\beta^2}=\mathrm{OC}$$

of the photo-electron, where β is the ratio of its velocity to that of light; and OF, the final momentum of the photo-atom.

According to our hypothesis, an impulse (represented by BC in fig. 1) acts upon the photo-electron to eject it. Hence the final momentum OC of the photo-electron may be thought of as consisting of three parts: OA, AB, and BC[17]. Accordingly we write the vector equation

$$\mathrm{OA}+\mathrm{AB}+\mathrm{BC}=\mathrm{OC}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we assume that the photo-atom acts as the seat of the reaction to the impulse BC, the final and initial momenta of the photo-atom differ vectorially by $\mathrm{DF}=-\mathrm{BC}$. This assumption is by no means necessary; for we might assume that the reaction to the impulse BC has its seat upon the source of the radiation, or upon the æther, or upon another electron[18], or we might even assume (as Lorentz has done under quite similar circumstances) that no reaction exists. Equation 1 is true, no matter which one of these views we may favour.

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[17] It is true that on the Bohr theory of the atom there is a binding force of electrostatic attraction between the nucleus and electron. The principal effect of this force is to abstract a certain amount of kinetic energy from the photo-electron by virtue of the distance through which the electron moves in escaping. But the time of escape is also a factor, for the more slowly the photo-electron escapes, the greater is the effect of the binding force in changing its direction of ejection. This is analogous to the effect of the speed of β-particles on their scattering by matter. The β-particles are supposed to travel in hyperbolæ, and to leave the centre of attraction with the same kinetic energy as that which they had before close approach. The entire effect of the attraction of the scattering nucleus (unless capture occurs) is to deflect the β-particle—the slower the β-particle the greater its deflexion. So far, comparison of our results with experiment does not oblige us to take account of the time of escape of the photo-electron in permitting the binding force to modify the direction of ejection of the photo-electron.

[18] Some photographs published recently (Proc. Roy. Soc. fig. 22, plate 12, civ. 1923) by C. T. R. Wilson may be interpreted as evidence for this view. These photographs show strange pairs of associated photo-electron tracks, both starting near the same point in the beam of X-rays and having about the same range. Now, if the photo-electron is ejected by a sideways impulse, it seems natural to look for evidence of an equal and opposite reaction impulse. We might suppose the quantum to exert a sideways impulse upon one electron, and its equal and opposite reaction impulse upon another electron, and consequently divide its energy about equally between the two. In this way we should get such pairs as Wilson finds. Wilson states that there is a great tendency for the line joining the points of origins of the two members of a pair to be nearly perpendicular to the primary X-ray beam. This observation is in accord with the present view. If the nucleus serves as the seat for the reaction impulse, it should receive, due to its great comparative mass, but a small part of the energy quantum. In this case we should get only one photo-electron—the ordinary case.

The principle of the conservation of energy requires that the energy of the system be the same before and after separation. Before separation the energy of the system consists of the quantum and the energy in the atom. After separation the energy consists of the kinetic energies of the photo-electron and photo-atom and the energy of the separated system. Accordingly, if w be the energy required to separate the photo-electron and photo-atom, and E the kinetic energy of the photo-atom [19], we have

$$h\nu = \mathrm{E} + mc^2(1/\sqrt{1-\beta^2}-1)+w. \quad . \quad . \quad . \quad (2)$$

We might write next the vector momentum equation OD − BC = OF for the photo-atom, and then eliminate BC from this equation and Eq. 1. The resulting equation could then be solved with Eq. 2 for the momenta of the photo-electron and photo-atom. However, this leads to rather complicated expressions, which may be avoided by dropping the negligible term E from Eq. 2. This term is negligible because the mass of the photo-atom is of the order 2000 times that of the photo-electron, and consequently its initial kinetic energy and change in kinetic energy are ordinarily of the order 1/2000 of the kinetic energy of the photo-electron. Dropping the term E from Eq. 2 gives

$$h\nu = mc^2(1/\sqrt{1-\beta^2}-1)+w, \quad . \quad . \quad . \quad . \quad (3)$$

which is the familiar Einstein photo-electric equation. It should be noted that although the kinetic energy of the photo-atom may be negligible in comparison with the kinetic energy of the photo-electron, the momentum change in the photo-atom is by no means negligible.

Statistical Considerations.

Since most experiments on the photo-electric effect are statistical in nature, we shall next consider the relations (1) and (3) as applied to such problems. In order to simplify the treatment, we shall make the following assumptions:—(*a*) The radiation ejecting the photo-electron is homogeneous. This requires ν to be constant. (*b*) The momentum vector of the electron in its atomic orbit is at random—that is, AB is random. (*c*) The momentum vector AB is constant in magnitude. This requires that all the photo-electrons be ejected from the circular K rings of the atoms. (*d*) The term w in Eq. 3 is constant in magnitude. This will be true if the condition (*c*) be satisfied, for then all photo-electrons will come from the same energy level.

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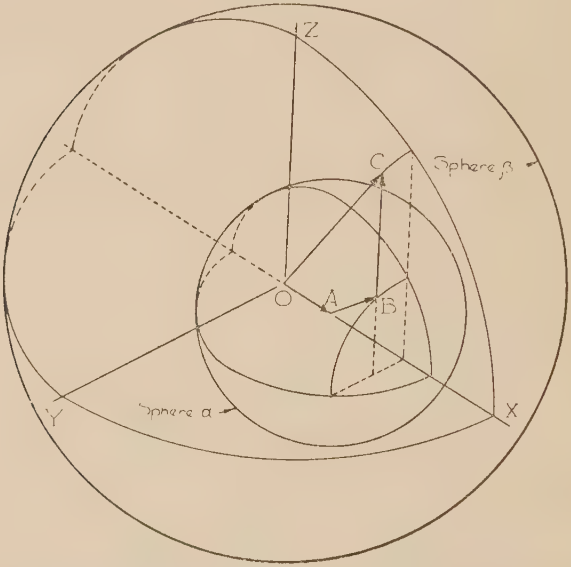
[19] Assuming that the reaction actually acts upon the photo-atom as the most likely hypothesis.

In the light of these restrictions let us reconsider fig. 1 and develop from it fig. 2. Since the initial momentum vector AB of the photo-electron is constant in magnitude and random in direction, the vector AB (see fig. 2) ends on a sphere (which we shall call α) of fixed centre A and radius

Fig. 2



Graphical representation of the momentum relations involved in the ejection of a large number of photo-electrons. This contains within its geometry many consequences of the present theory.

$$\mathrm{AB}=m\beta_0 c/\sqrt{1-\beta_0^2}.$$

From the restrictions (*a*) and (*d*) and Eq. 3 it is easy to see that the final momentum vector

$$\mathrm{OC}=m\beta c/\sqrt{1-\beta^2}$$

is constant in magnitude, and hence ends on a sphere (which we shall call β) of fixed centre O and radius

$$\mathrm{OC}=\sqrt{(mc^2+h\nu-w)-m^2c^4}/c.$$

Although the point B is at random on sphere α, the point C is not at random on sphere β; for by hypothesis the impulse BC is parallel to OZ. Hence point C is to be located by finding the point of intersection of sphere β with a line drawn through B parallel to OZ.

These various relations are exhibited in fig. 2, which contains within its geometry many of the immediately useful results of the present theory.

Applications of the Theory to Experiments.

Longitudinal Asymmetry.—In fig. 2 let the YZ plane represent a thin plate or film of matter traversed by unpolarized radiation proceeding in the direction OX. The photo-electrons which are ejected from the plate may be divided into two classes: those leaving the plate on the forward or emergent side (positive side of YZ plane), and those leaving the plate on the backward or incident side. It is the ratio of the forward to the backward photo-electric current which Bragg, Cooksey, and Beatty measured in their experiments mentioned above. We proceed to calculate this ratio in view of the present theory.

From fig. 2 it is clear that all the photo-electrons of the forward class have their final momentum vectors OC ending on that portion of sphere β to the right of the YZ plane, and their initial momentum vectors AB ending on that portion of sphere α to the right of the YZ plane. Similarly, all photo-electrons of the backward class have their final and initial momentum vectors ending respectively on those zones of spheres β and α to the left of the YZ plane. If we suppose that we are dealing with a sufficiently great number of photo-electrons to justify a statistical treatment, we can say that the ratio R of forward to backward photo-electric current is equal to the ratio of the area of the zone of sphere α on the right of the YZ plane to the area of the zone of sphere α on the left of the YZ plane. But these areas are in the ratio of their altitudes, from which we get the equation

$$R = (AB + OA) / (AB - OA). \quad . \quad . \quad . \quad (4)$$

The initial momentum AB of the electron in its atomic orbit may be expressed in terms of its energy of binding $h\nu_0$ by the formula[20]

$$AB = m\beta_0 c / \sqrt{1-\beta_0^2} = mc\sqrt{2\alpha_0 - \alpha_0^2} / (1-\alpha_0), \qquad (5)$$

[20] Calculated on the basis of the Bohr theory of the atom for circular orbits only, such as the K rings. For circular orbits the momentum of the electron in its atomic orbit is constant as demanded by our restriction (*c*). For elliptical orbits our momentum vector AB would not be constant in magnitude.

where $\alpha_0 = h\nu_0/mc^2$. Remembering that $OA = h\nu/c$ and letting $\alpha = h\nu/mc^2$ and substituting Eq. 5 in Eq. 4, we get

$$R = \{\sqrt{2\alpha_0 - \alpha_0^2} + \alpha(1-\alpha_0)\} / \{\sqrt{2\alpha_0 - \alpha_0^2} - \alpha(1-\alpha_0)\}. \quad (6)$$

Putting in the numerical values of h, m, and c and expressing λ and λ_0 in Ångström units, we have, finally,

$$R = \{\lambda\sqrt{82 \cdot 44\lambda_0 - 1} + \lambda_0 - 0 \cdot 0242\} / \{\lambda\sqrt{82 \cdot 44\lambda_0 - 1} - \lambda_0 + 0 \cdot 0242\}, \quad (7)$$

where λ is the wave-length in Å. of the radiation ejecting the photo-electrons, and λ_0 is the critical ionization wave-length in Å. of the atom from which the photo-electrons are ejected. A fairly complete list of the critical ionization wave-lengths for various atoms has been tabulated by Duane[21].

The Eq. 7 is subject to the condition that the quantum $h\nu$ possess sufficient energy to eject the photo-electron—that is, we must have

$$\lambda < \lambda_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In Bragg's experiments[2] on this longitudinal asymmetry, the source of the radiation (gamma rays) was held constant (λ constant) while the source of the photo-electrons was varied (λ_0 varies). The ratios as determined experimentally by Bragg for various substances are considerably smaller than the corresponding theoretical ratios as calculated from Eq. 7. However, this is to be expected since Bragg used very thick plates. In the first place, photo-electrons ejected from layers inside a thick plate must suffer many deflexions in passing out. It is not difficult to see that this tends to cut down the forward and increase the backward photo-electrons. Again, thick plates absorb the radiation as well as the photo-electrons, so that if the plate were sufficiently thick we should get nothing out of it except incident photo-electrons. Indeed, Rutherford[22], in considering the effect of scattering of the photo-electrons by thick plates, regards Bragg's results as conflicting in no way with the assumption that all the photo-electrons are ejected initially in the direction of the radiation. A comparison of theoretical with these experimental ratios brings out the essential agreement that both increase as the atomic number of the source of the photo-electrons decreases.

In Beatty's experiments[6] the source of the photo-electrons

[21] Duane, Bull. Nat. Res. Coun. no. 6 (1920).

[22] Rutherford, 'Radioactive Substances and their Radiation,' p. 275.

was held constant and the wave-lengths of his homogeneous X-rays were varied. A comparison brings out the additional essential agreement that R increases as the hardness of the radiation increases. In these results the theoretical ratio again exceeds the experimental. The reason is again probably because the plates were too thick. Beatty's source of photo-electrons was a film of silver estimated to be 1100 atoms thick.

Cooksey's results[5], shown in Table I., may be expected to furnish a more rigorous test of the present theory. Cooksey determined the ratios for various thicknesses of plate, and extrapolated to find the ratio corresponding to zero thickness. These extrapolated ratios are given together with the corresponding theoretical ratios in Table I. These results are seen to be in good agreement numerically.

Table I.

Source of Radiation.	Source of Photo-electrons.			
	Gold.		Silver.	
	R exp.	R cal.	R exp.	R cal.
Chromium	1·20	1·23	1·24	1·20
Iron	1·24	1·28	1·21	1·24
Zinc	1·21	1·21	1·20	1·34
Tin	1·16	1·51	1·23	1·37

In some recent experiments by O. K. de Foe[23] this ratio was measured by counting the forward and backward tracks produced inside a Wilson cloud expansion apparatus by the homogeneous K_α radiation from molybdenum. The experimental ratio thus found was 2·89, while the theoretical ratio according to Eq. 7 is 3·38. These values agree within 15 per cent., which seems to be good evidence for the present theory.

Lateral Asymmetry.—Suppose a photographic plate to be erected parallel to the YZ plane of fig. 1—that is, normal to the direction OX of the radiation ejecting the photo-electrons. We wish to calculate the distribution, as regards initial direction of ejection of the photo-electrons ejected by polarized radiation, appearing on a Wilson cloud photograph on such a plate. The writer has performed an experiment[8] with the apparatus thus briefly outlined in which the radiation along the OX axis was plane polarized with the electric vector parallel to the OZ axis. A strong concentration of photo-electrons ejected nearly parallel to the electric vector was discovered.

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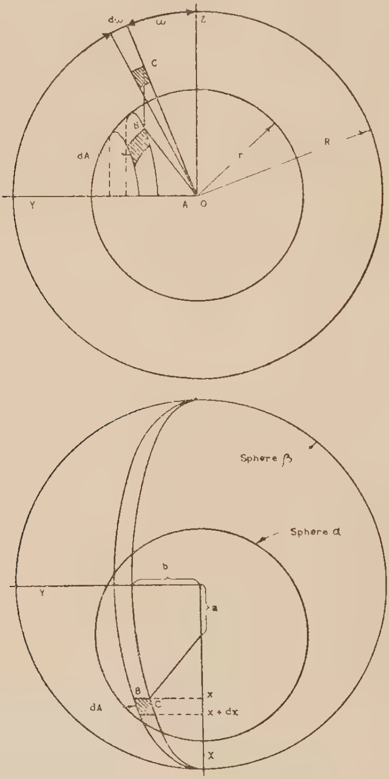
[23] See present issue of the Phil. Mag. p. 817.

Fig. 3.



The momentum relations involved in the ejection of a large number of photo-electrons by polarized radiation.

Pass two planes through the line OX making the angle $d\omega$ with each other and the angle ω with the XZ plane. These two planes cut the sphere β in two great circles which bound a lune on the surface of sphere β. Let us represent the projections of spheres α and β upon the XY and YZ planes, somewhat as the engineer shows a plan and elevation (see fig. 3). The projection of the lune defined above is shown on the XY plane as bounded by two ellipses, and its projection upon the YZ plane as two radii.

All photo-electrons whose final momentum vectors OC end on the lune have their initial momentum vectors AB ending on a small area of sphere α, which is bounded by two skew curves. These two skew curves are the projections on α of the two great circles on β, and are defined by projectors all of which lie on the surface of an elliptical cylinder whose elements are parallel to the OZ axis. These curves are hidden by the ellipses in the plan, but appear separately in the elevation.

Since a sufficiently large number of tracks will give a uniform distribution of initial momentum vectors AB over the surface of α, it is clear that the relative number of tracks on the photographs whose initial portions lie within the angle $d\omega$ to the total number of tracks is equal to the ratio of one of these elementary areas on α to the whole area of α. The two projecting cylinders cut two elementary areas out of α, one on the upper and one on the lower hemisphere. Since each of these may be supposed to contribute only one-half its photo-electrons to the lune (the other halves going to a symmetrical lune on the lower hemisphere of β), the element to be used in the above ratio may be taken as that on one hemisphere of α.

It therefore becomes necessary to calculate one of these elementary areas of α. Pass two planes perpendicular to the OX axis, one at x and the other at $x+dx$. Each plane cuts a circle from α. These two circles cross both skew curves on α, and thereby bound a small area which we shall call $d\mathrm{A}$. The projection of $d\mathrm{A}$ upon the XY plane is bounded by two infinitesimal straight lines and two infinitesimal elliptical arcs. We shall call this projected area $d\mathrm{A}'$. We have at once

$$d\mathrm{A}' = dx\,dy,$$

where y is given by the ellipse

$$y = \sqrt{\mathrm{R}^2 - x^2}\sin\omega.$$

Accordingly we have

$$d\mathrm{A}' = \sqrt{\mathrm{R}^2 - x^2}\cos\omega\,d\omega\,dx.$$

Supposing $d\mathrm{A}$ to be so small that second-order terms may be neglected, the angle between the "plane" $d\mathrm{A}$ and its projection $d\mathrm{A}'$ has for its cosine the value z/r. Hence we have

$$d\mathrm{A} = r\sqrt{\mathrm{R}^2 - x^2}\cos\omega\,d\omega\,dx\,/\,z,$$

in which, besides the variable x, there appears nothing but z. The variable z may be expressed in terms of x by eliminating y between the equation of the ellipse given above and the sphere

$$z^2+y^2+(x-a)^2=r^2.$$

Hence we have finally

$$dA=r\sqrt{R^2-x^2}\,d\omega\,dx\,/\sqrt{A^2-(x-B)^2},$$

where
$$A^2=\sec^2\omega(r^2+a^2\tan^2\omega-R^2\sin^2\omega)$$

and
$$B=a\sec^2\omega.$$

The limits between which dA is to be summed are x_1 and x_2, the two roots of x found by solving simultaneously the ellipse and circle given by the respective equations

$$y=\sqrt{R^2-x^2}\sin\omega \quad \text{and} \quad y^2+(x-a)^2=r^2.$$

This gives
$$x_1=B-A \quad \text{and} \quad x_2=B+A.$$

Since the number of tracks per unit area is $N/4\pi r^2$, we have finally

$$dN/d\omega=N/4\pi r\int_{B-A}^{B+A}\sqrt{R^2-x^2}\,dx/\sqrt{A^2-(x-B)^2}. \quad (9)$$

After some reduction this expression becomes

$$\begin{aligned}dN/d\omega&\\ =N/4\pi r\{&F(\pi/2,k)(R-A-B)\sqrt{(R+A-B)/(R+A+B)}\\ &+E(\pi/2,k)\sqrt{(R+A-B)(R+A+B)}\\ &+\Pi(\pi/2,n,k)2B(R-A-B)\,/\,\sqrt{(R+A)^2-B^2}\},\end{aligned} \quad (10)$$

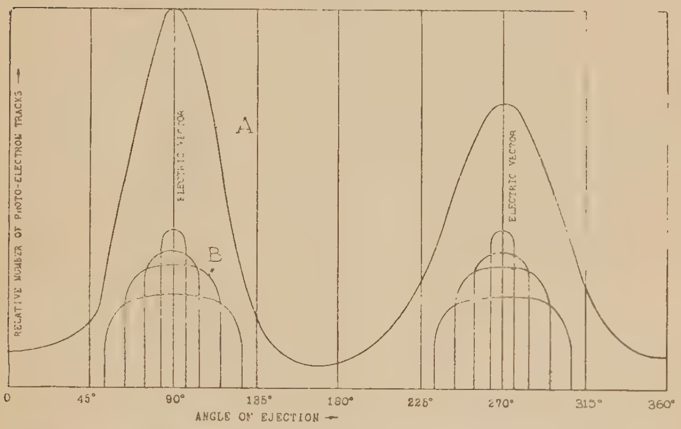
where $F(\pi/2,k)$, $E(\pi/2,k)$, and $\Pi(\pi/2,n,k)$ are the complete elliptical integrals of the first, second, and third kinds respectively. The modulus

$$k=2\sqrt{AR/[(R+A)^2-B^2]},$$

and the parameter
$$n=-2A/(R+A-B).$$

Fig. 4 furnishes a comparison between an experimental curve[8] and several curves calculated from theory. Curve A shows the relative number of photo-electrons ejected at all angles by heterogeneous polarized X-rays. The source of the X-rays was a Coolidge tube with a tungsten target operated at about 50,000 volts by a transformer. The X-rays were polarized by scattering from a paraffin block at 90°. Curves B were calculated from Eq. 9 by graphical integration. Each of the curves B represents the theoretical distribution for a homogeneous radiation ejecting electrons from the nitrogen K ring. The width of a particular curve depends on the hardness of the radiation—the harder the radiation, the narrower the hump. The height of a particular hump depends on the intensity of the corresponding radiation. Several of these curves are shown for the purpose of bringing out the possibility that the curve A is the sum of a number of such curves B corresponding to the various lengths of X-rays making up the heterogeneous beam used in obtaining the curve A. The Eq. 9 requires that the radiation producing the ejection be homogeneous, and also that all photo-electrons come from the same energy level. In order, then, to calculate a curve to compare with curve A, it is necessary to know the wave-length and intensity of all the radiation as well as the relative number of photo-electrons

Fig. 4.



Comparison of experimental and theoretical curves, showing the distribution of photo-electrons ejected by plane polarized radiation.

ejected from the various gases—nitrogen, oxygen, argon, etc.—which were present in the expansion chamber. The comparison presented in fig. 4 is then only for the purpose of showing qualitative agreement. Experiments are in progress in which it is hoped to settle the question of quantitative agreement.

Discussion.

The present theory admits of a number of tests, only three of which have been considered here. The experiments of Bragg and Beatty on the Mackensie asymmetry give qualitative support to the theory, in that the theoretical ratio of forward to backward photo-electric current varies both with hardness of the radiation and with source of the photo-electrons in the same way as the experimental ratio varies The experiments of Cooksey and of de Foe on the same asymmetry are in close numerical agreement with the predictions of the theory. The writer's experiments with polarized X-rays, in which the tendency for the photo-electrons to proceed in the direction of the electric vector was discovered, also support the theory qualitatively. The theory further agrees with the results of Beatty and Piersol, in that it predicts the velocity of ejection to be independent of the direction of ejection.

A number of additional predictions of the theory have been omitted from the present paper, since experimental work in progress for the purpose of testing them has not been carried far enough. In particular, we mention that the theory offers certain information on the time of action between the quantum and electron when the binding force between the electron and nucleus is taken account of.

Apart from the well-known difficulties which the wave theory has in explaining the Einstein photo-electric relation, the present theory introduces nothing contradictory to the wave theory. If we favour the corpuscular viewpoint, however, it appears that the orthodox view of the quantum as a scalar bundle of energy must be modified to account for the lateral asymmetry in the direction of ejection of photo-electrons. We may view the quantum as a "vector quantum," since it appears to exert a sideways impulse to eject the photo-electron.

LXXXVIII. *On the Universal Distance of the Order of 10^{-8} cm. between the Centres of Nearest Atoms.* By ALBERT C. CREHORE *.

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I. *Introductory.*

THIS title has been chosen to emphasize a well-known experimental result of crystal analysis, which is seldom stressed, but which is of the utmost importance and is the key to the proper understanding of the structure and behaviour of atoms. The distance between centres of the nearest adjacent atoms in crystals is in round numbers found experimentally to be of the order of 10^{-8} cm. rather than 10^{-7}, 10^{-9}, or 10^{-10} cm. It may be as small as $\cdot 5\times 10^{-8}$ cm. or as large as 4×10^{-8} cm. in special cases perhaps, but the minimum distance always falls within these rather narrow limits. Considering the very small size of the electron itself, which is now experimentally established, the experimental and theoretical dimensions agreeing very satisfactorily, and taking into account that this negative electron is the largest fundamental body of charge that enters into the structure of an atom, for the negative electron occupies a far greater volume than any positive charge: taking these things into consideration, it is not at all evident why 10^{-8} cm. instead of 10^{-7} or 10^{-9} cm. should have been this universal distance. There appears to be plenty of room for distances much smaller or greater than 10^{-8} cm., and it has not been evident why there should exist such a universal distance of any value whatever.

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* Communicated by the Author.

But it is evident from the same facts that there must exist a very definite causal connexion between the constitution or structure of the atoms themselves and this universal distance, for with so many different kinds of atoms one might expect a much wider departure from 10^{-8} cm. than is found experimentally, if there exists no controlling principle within each atom. If, however, it can be shown that this universal distance is closely related to the properties of the atom and negative electron itself and controlled by them, as is shown in this paper, it is not surprising but very natural to expect a universal distance between atomic centres, because the electron forms an integral part of each and every one of these atoms. The main distance itself between the atoms will then be determined by the negative electron, and the very small variations from this main distance will depend upon the particular grouping of these electrons within each atom in the different kinds of atoms.

This subject has been treated in a preliminary way in former papers* from the standpoint of a new atomic model based upon electrodynamics, in which there are no electronic orbits in the steady state of atoms. It is not intended to open this question again here as to whether or not there exist any such steady orbits, but rather to give an account of progress in the mathematical investigation of the new atomic model, with particular reference to this universal distance, above mentioned, of the order of 10^{-8} cm.

Without departing at the outset from the doctrine of electromagnetic theory, no such orbits of negative electrons are admissible in atoms in their steady states, but it is not intended to abandon electrodynamics at any point. Moreover, such a course is not at all necessary. These orbits are not needed. On the other hand, those who have become accustomed to think in terms of orbits may easily attribute the universal distance of 10^{-8} cm. to the dimensions of the orbits themselves, which have been computed by means of this same electrodynamics that was abandoned in the matter of radiation of energy from electrons describing orbits. When one pictures a crystal model based upon the stationary-orbit-form of atom, where the revolving electrons come very close together at certain points and depart far asunder again at other points, and realizes that it is necessary to postulate no mutual reaction between these orbital electrons such as electromagnetic theory demands, it seems that the time has arrived to search for a more satisfactory form of atomic model, one that does not abandon electrodynamics at the outset.

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* A. C. Crehore, Phil. Mag. p. 569, Oct. 1921; p. 886, May 1922; p. 1025, June 1922; p. 33, Jan. 1923.

Quite apart from all thoughts as to the actuality of things, the mathematical aspects of the problem suggested by the new atomic model, with which we are concerned, have many features of great beauty and sufficient merit to maintain the interest, to say nothing of the new field that has been opened for atomic physics. How to give readers an understanding of the subject with the minimum of effort on their part has received some study. The historical order of development would be the easiest, but an objection is that the results become clouded with a mass of detail. It has been necessary, however, to pass through many successive steps to attain the final result to be described, and if these steps were omitted there is a question whether the presentation would have much meaning or be understood.

Let us begin by restating some of the properties of the fundamental bodies, the negative electron and the positive charge of the hydrogen atom, with which the atom and then the molecule of hydrogen are built, as before given in the first paper*. The negative electron in its free state when not forming a part of an atom is supposed to be an oblate spheroid of negative charge $(-e)$ in rotation about its minor axis. The charge is supposed distributed uniformly throughout the volume, which is the equivalent of a sphere of radius

$$r=2{\cdot}244\times10^{-13}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The semi-axes of the meridian section are

$$\left.\begin{aligned} a&=3{\cdot}257\times10^{-13}\text{ cm.,}\\ b&=1{\cdot}065\times10^{-13}\text{ cm.,}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

and the eccentricity

$$\epsilon=0{\cdot}945. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

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* *Loc. cit.* Phil. Mag. October 1921, p. 589.

The total energy content of the negative electron is equivalent to its mass times the square of the velocity of light. Denoting its mass at zero translational velocity by m_0 and the velocity of light by c, it becomes

$$E_0=0{\cdot}898\times10^{-27}\,c^2=8{\cdot}08\times10^{-7}\text{ erg.} \quad . \quad . \quad (4)$$

The positive charge of the hydrogen atom is supposed to be an oblate spheroid with uniformly distributed charge having the same eccentricity as the negative electron, (3) above. But its charge is $+2e$ instead of $-e$ and its dimensions are equivalent in volume to a sphere of radius

$$r=4{\cdot}86\times10^{-16}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The semi-axes are

$$\left.\begin{aligned} a&=7{\cdot}054\times10^{-16}\text{ cm.,}\\ b&=2{\cdot}307\times10^{-16}\text{ cm.}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

The total energy content of this positive charge is also given by the product of its mass by the square of the velocity of light, namely

$$E=1{\cdot}66\times10^{-24}\,c^2=1{\cdot}49\times10^{-3}\text{ erg.} \quad . \quad . \quad (7)$$

For comparison it is important to bear in mind that the energy required to separate the two atoms of hydrogen forming one molecule to a great distance from each other is

$$E=5{\cdot}8\times10^{-24}\text{ erg.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This value has been determined experimentally due to Langmuir, and the order of magnitude of most of the energies of the heats of formation and heats of dissociation in many chemical reactions is well represented by this figure.

The energy content of the negative electron is more than 100,000 times this value, and of the positive charge more than 250,000,000 times it. These facts have a very important bearing upon the whole behaviour of atoms. It seems best to give at the outset the reasoning that shows the important part played by the very large energy content of the electron in the formation of atoms and of molecules. The oblate spheroid given by (2) is supposed to be that of a free electron which is in stable dynamic equilibrium. Two such electrons will be attracted by the positive charge ($2e$) of a hydrogen atom at all distances, and will approach it until they come into contact with it, the three bodies aligning themselves on a common axis as in fig. 1, which represents a meridian section of a hydrogen atom *.

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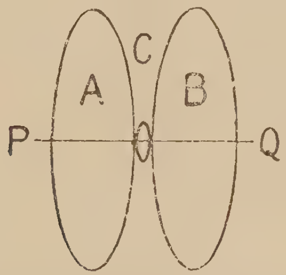
* *Loc. cit.* p. 588.

The pressure of each electron upon the positive charge due to the resultant attraction of the other two bodies must cause a slight flattening of the original figure of the free electron. But to either flatten or to expand the figure of the free electron, which is in dynamic equilibrium, requires that work be done, and, if the amount of this change of shape were known, the energy may be computed, or *vice versa*, if the work done were known, the change in shape may be computed. Now the energy so involved represents the difference between the energies of the free bodies and these same bodies as they exist in the atom, that is to say, it is the energy of ionization of the free hydrogen atom.

Fig. 1.



Meridian section of the hydrogen atom described in the first paper.

But there are two energies of ionization for an atom which carries two electrons—the first when only one electron is detached, and the second when both are detached. The first of these is the only one that has ever been measured for hydrogen, and this will be of little service to us. The second energy must be far greater than the one which has been measured. In fact, it figures so great that the last electron never leaves the positive charge, at least in laboratory experiments so far conducted, and so it cannot of course be measured. And so we have never heard of a hydrogen ion with two positive charges. The maximum it has been possible to give it in the laboratory is one positive charge.

It seems profitable to picture the change that takes place in the atom during the removal of one electron. Were it not for the fact that much of the energy of the electron on the opposite side is transferred over to the one electron during the process of removal of the one, it would not be possible to remove even one, for in the symmetrical position in the free atom of course each electron shares alike and represents one-half of the very large energy of the double ionization. But, when one begins to move away from the centre of the atom, its minor axis expands because of the release of the pressure, and thereby it gives up some of the energy that was expended upon it during the formation of the atom. At the same time the minor axis of the opposite electron must contract slightly because of the increased pressure on that side due to the removal of the first electron, and thus it is apparent that there is a transfer of some of the energy across from the one to the other electron.

The comparatively small difference between the gain of energy of the one that remains and the loss of energy of the one that departs represents the rather small energy of the first ionization of the hydrogen atom. This is known experimentally, but is not of much importance for this problem. The more important energy, which is not known experimentally and probably will not be measured for some time to come, is the second or total ionization energy.

It seems important, however, to attack the problem from the standpoint of energy; and we shall now consider the problem of finding a relation between the energy absorbed or emitted by a negative electron because of a definite change in its semi-minor axis. When the hydrogen atom is formed as in fig. 1 because each electron is attracted at all distances until they both come into actual contact with the positive charge, then the attraction, which still continues, results in a deformation of the shape of the electron. It may be assumed, since this change is extremely small for a comparatively large energy change, that each remains an oblate spheroid as before. The result of the pressure between the electron and the positive charge is to flatten the spheroid slightly, thus increasing its eccentricity and decreasing its semi-minor axis.

II. *The Change in the Energy Content of the Electron for a Given Change in the Semi-minor Axis.*

It will be assumed as before that the volume of the spheroid, which has a uniform distribution of charge throughout, remains constant and fixed, equal to that of a sphere of radius r, given by (1) above. This volume is

$$V = \tfrac{4}{3}\pi r^3. \qquad \qquad (9)$$

The volume of an oblate spheroid of polar semi-axis b and equatorial radius a_0 is

$$V = \tfrac{4}{3}\pi a_0^2 b. \qquad \qquad (10)$$

Equating these volumes gives an immediate relation between a_0 and b:

$$a_0^2 b = r^3 \quad \text{or} \quad \frac{b^2}{a_0^2} = \frac{b^3}{r^3}. \quad . \quad . \quad . \quad . \quad (11)$$

But in an ellipse the relation between the axes and the eccentricity is

$$\frac{b^2}{a_0^2} = 1-\epsilon^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Whence, equating (11) and (12), we have

$$\frac{b^3}{r^3} = 1-\epsilon^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The area of an oblate spheroid S in terms of its semi-axes and eccentricity is

$$S = 2\pi a_0^2 + \frac{\pi b^2}{\epsilon} \log \frac{1+\epsilon}{1-\epsilon}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

By means of the above relations this area is expressible in terms of the eccentricity alone, as

$$S = 2\pi r^2 \left[(1-\epsilon^2)^{-1/3} + \frac{1}{2\epsilon}(1-\epsilon^2)^{2/3} \log \frac{1+\epsilon}{1-\epsilon} \right]. \quad (15)$$

From this we wish to find the change in the area of the spheroid that corresponds to a given change in the minor axis; and since this change is extremely small, the differential of S may be used. Differentiating (15) with respect to ϵ gives

$$\frac{dS}{d\epsilon} = 2\pi r^2 \left\{ \frac{2}{3}(1-\epsilon^2)^{-4/3} + \frac{1}{\epsilon}(1-\epsilon^2)^{-1/3} \right.$$
$$\left. - \left[\frac{2}{3}(1-\epsilon^2)^{-1/3} + \frac{1}{2\epsilon^2}(1-\epsilon^2)^{2/3} \right] \log \frac{1+\epsilon}{1-\epsilon} \right\}, \quad (16)$$

which in terms of r, b, and ϵ is equivalent to

$$\frac{dS}{d\epsilon} = 2\pi r^2 \left\{ \frac{2}{3}\left(\frac{r}{b}\right)^4 + \frac{1}{\epsilon}\left(\frac{r}{b}\right) - \left[\frac{2}{3}\left(\frac{r}{b}\right) + \frac{1}{2\epsilon^2}\left(\frac{b}{r}\right)^2 \right] \log \frac{1+\epsilon}{1-\epsilon} \right\},$$
$$. \quad . \quad . \quad (17)$$

By means of (13) the rate of change of ϵ with respect to b may be obtained by differentiation as follows:

$$\frac{d\epsilon}{db} = -\frac{3}{2\epsilon r}(1-\epsilon^2)^{2/3} = -\frac{3b^2}{2r^3\epsilon}. \quad . \quad . \quad . \quad (18)$$

The rate of change of the area of the spheroid S with respect to the semi-minor axis b is then the product of (17) by (18). Denoting the brace in equation (17) by $f(b)$ for brevity, we obtain

$$\frac{dS}{db}=\frac{dS}{d\epsilon}\cdot\frac{d\epsilon}{db}=-\frac{3\pi b^2}{r\epsilon}f(b). \quad . \quad . \quad . \quad . \quad (19)$$

When the change in area is small, we may say that dS becomes $\Delta S=S_2-S$, and db becomes $\Delta b=b_2-b$; whence

$$S_2-S=-\frac{3\pi b^2}{r\epsilon}(b_2-b)f(b). \quad . \quad . \quad . \quad . \quad (20)$$

In accord with the properties of the electron as given in the first paper (see equation (73)), there is a surface tension over the entire surface of the electron given by

$$T=\frac{3}{16}\frac{e^2}{\pi r^2 k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

To increase its surface by the amount S_2-S and to flatten the electron, thus reducing its minor axis, requires an amount of energy

$$\Delta E=T.\Delta S=T(S_2-S). \quad . \quad . \quad . \quad . \quad (22)$$

Hence by (20) and (21)

$$\Delta E=-\frac{9}{16}\frac{b^2e^2}{r^3\epsilon k}(b_2-b)f(b). \quad . \quad . \quad . \quad (23)$$

Taking b in round numbers as 10^{-13} cm., and r as given by (1), the eccentricity obtained from (13) is

$$\epsilon=0{\cdot}9547. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

So by (23) we find numerically that

$$\Delta E=-\frac{e^2}{k}({\cdot}307\times10^{26})(b_2-b). \quad . \quad . \quad . \quad (25)$$

Using as the value of the charge, $e=4{\cdot}763\times10^{-10}$ E.S.U., the energy in (25) becomes

$$\Delta E=-6{\cdot}964\times10^6(b_2-b), \quad . \quad . \quad . \quad . \quad (26)$$

which is the expression that was to be found.

III. *The Energy of Double Ionization of the Hydrogen Atom.*

In the free state of the electron the value of b given by (2) above is $1{\cdot}065\times10^{-13}$ cm. If this is contracted down to exactly 10^{-13} when the hydrogen atom is formed, it would mean that

$$b_2-b=(1-1{\cdot}065)\times10^{-13}=-0{\cdot}065\times10^{-13}\text{ cm.} \quad (27)$$

The corresponding energy change by (26) becomes

$$\Delta E = 0{\cdot}4527 \times 10^{-7} \text{ erg}, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and according to (4) above, this is the 1/17·85 part of the total energy content of the negative electron. This would make the total energy of double ionization of the free hydrogen atom double this figure, since in the free atom the two electrons are supposedly symmetrical. The numerical value thus obtained is probably much too great, and the reason for giving it is to show that the contraction of the semi-minor axis is probably much less than from 1·065 down to 1×10^{-13} cm. as arbitrarily assumed. However, since the experimental value of this is unknown, it may be assumed without affecting any of the results that follow appreciably that $b = 10^{-13}$ cm. in round numbers, and that the eccentricity is 0·9547 in the free hydrogen atom as computed.

IV. *The Hydrogen Molecule.*

Let us first consider in a general preliminary way the formation of the hydrogen molecule by the uniting of two hydrogen atoms. The first striking result of an application of the equations expressing the forces which are given below is that the second atom exerts a very large force in one direction upon the two negative electrons of the atom, and a correspondingly large force upon the positive charge of the atom in the opposite direction. The effect of these larger forces is necessarily to change the pressure between the electrons and the positive charge as well as to displace very slightly the location of the positive charge to one side of the centre-line of the two electrons. These larger forces, in other words, have the effect of slightly deforming the atom itself, so that it is no longer a symmetrical atom as it exists in the free state. We really have to deal with a slightly different atom when it forms part of a molecule as well as during the process of formation of the molecule than when free.

It required some time and experience to realize that these deformations are of any practical importance, since they are evidently very small effects. The reason why they become important, when examined in terms of the equations expressing the electrostatic forces between the fundamental bodies, is because the asymmetry of the deformed atom introduces new terms in the lower orders of the distance between centres of the two atoms of the molecule, denoted by r. Recalling that the forces are necessarily expressed by an infinite series in terms of r^{-2}, r^{-3}, r^{-4}, etc., and remembering that the series is so rapidly convergent that each term is nearly 10^5 times smaller than the preceding term, unless some special condition is imposed upon the coefficients of the terms, it appears that ordinarily the first term of the series represents the sum of all its terms to a close approximation. When the two atoms are each symmetrical with respect to an axis and centre, it results that all the odd powers of r have vanishing coefficients in the series expressing the total electrostatic force of a second atom upon the first. And besides this, all coefficients vanish up to but not including the r^{-6} term. Hence the first term of the series is the r^{-6} term, which would represent practically the whole force unless its coefficient is modified by some condition connected with the form of the electron. The next term of this series for a symmetrical atom is the r^{-8} term, which is ordinarily 10^{10} times smaller than the r^5 term and is of no value.

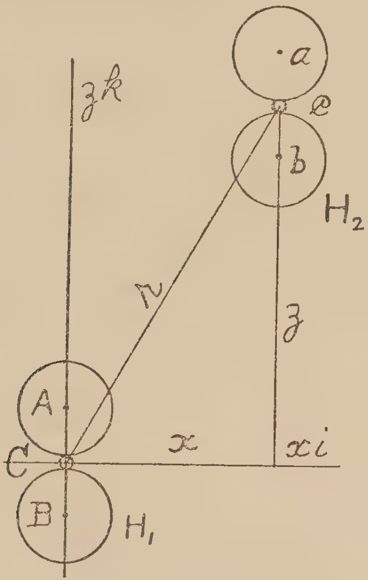
With a deformed atom, however, not only do earlier terms appear of lower orders in r, but the odd powers are present as well, the small coefficients of the earlier terms giving values that compare on equal terms with the important r^{-6} term above mentioned, and they are therefore not to be neglected.

This matter may be understood so much more readily when the equations referred to are before us that it seems best to give them at once, and they will be given in progressive steps of approximation to the model of the atom of fig. 1. It is regretted that there is not space to give all the details of their derivation; but to do this would not only extend the paper to great lengths, but might at the same time obscure the purpose and aims of the whole. So results only are given in this paper, but the processes are clearly indicated.

V. *The Spherical Electron in a Symmetrical Atom.*

As a beginning let it be supposed that each fundamental charge in the atom has a spherical shape, and that each atom is symmetrical with respect to its central point, in order that comparisons may be made later and the effect of non-spheres and asymmetry noted. A diagram of the atoms of the hydrogen molecule would then be represented as in fig. 2. Each charge may be treated mathematically as though it were all concentrated at the centre of its respective sphere. The centre of the first atom, H_1, composed of two negative electrons, A and B, and one positive charge, C, is located with its centre at the origin of coordinates, the z- or k-axis taking the polar and the x- or i-axis the equatorial direction. The centre of the second atom, H_2, is located in any general position at the point (x, z), but its axis, which in the final model is an axis of rotation for each fundamental body, is shown as parallel to that of the first atom, H_1, that is parallel to the z-axis.

Fig. 2.



Hydrogen molecule assuming spherical electrons.

The distance between the centres of A and C, B and C, a and c, and b and c may be denoted by b, which is very closely equal to the radius of the negative electron ; and the distance between the centre of the second atom, namely c, and the centre of the first, namely C, may be denoted by r.

The direction cosines defining the position of the centre of the second atom with respect to the first may be denoted by

$$X = x/r \quad \text{and} \quad Z = z/r. \quad . \quad . \quad . \quad . \qquad (29)$$

Then it may be shown that according to the inverse-square-law of electrostatic force, the force upon the positive charge $C = 2e$ of the first atom due to the sum of the forces of both *a* and *b* of the second atom is given by the two components resolved along the *x*- and *z*-axes as follows :

$$\underset{a+b \text{ on C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}[4r^{-2}-6b^2r^{-4}f_{x,4}(\mathrm{Z})+\tfrac{15}{2}b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots], \quad (30)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}[4r^{-2}-6b^2r^{-4}f_{z,4}(\mathrm{Z})+\tfrac{5}{2}b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots], \quad (31)$$

where

$$f_{x,4} = 1-5\mathrm{Z}^2, \quad (32)$$

$$f_{z,4} = 3-5\mathrm{Z}^2, \quad (33)$$

$$f_{x,6} = 1-14\mathrm{Z}^2+21\mathrm{Z}^4, \quad (34)$$

$$f_{z,6} = 15-70\mathrm{Z}^2+63\mathrm{Z}^4. \quad (35)$$

When positive, these represent attractive forces.

The force upon the two negative electrons, A and B together, of the first atom due to the two, *a* and *b* together, of the second atom is given by

$$\underset{\substack{a+b \\ \text{on A+B}}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}[-4r^{-2}+12b^2r^{-4}f_{x,4}(\mathrm{Z})-60b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots], \quad (36)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}[-4r^{-2}+12b^2r^{-4}f_{z,4}(\mathrm{Z})-20b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots]. \quad (37)$$

The force upon C of the first atom due to *c* of the second is simply

$$\underset{c \text{ on C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}(-4r^{-2}), \quad (38)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}(-4r^{-2}). \quad (39)$$

The force of the whole atom H_2 upon the positive charge C of the first atom is evidently the sum of (30) and (38) for the *x*-component, and of (31) and (39) for the *z*-component. It is not necessary to write this down, because the result is the same as (30) and (31) when the r^{-2} terms are omitted.

The force of the whole atom H_2 upon the two electrons A and B of the first atom is evidently the sum of (30) and (36) for the *x*-component, and of (31) and (37) for the *z*-component, since the force of *a* plus *b* upon C is evidently the same as that of c on A plus B. This sum is

$$\underset{\mathrm{H_2\ on\ A+B}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\left[6b^2r^{-4}f_{x,4}(\mathrm{Z}) - \tfrac{105}{2}b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots\right], \quad . \quad (40)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\left[6b^2r^{-4}f_{z,4}(\mathrm{Z}) - \tfrac{35}{2}b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots\right], \quad . \quad (41)$$

where the Z-functions are given by (32) to (35) inclusive.

The force upon the whole first atom due to the second is then the sum of (30) and (40) for the x-component, and of (31) and (41) for the z-component, remembering to omit the r^{-2} terms of (30) and (31) as pointed out above. Hence we have

$$\underset{\mathrm{H_2\ on\ H_1}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\left[-45b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots\right], \quad . \quad . \quad . \quad (42)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\left[-15b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots\right]. \quad . \quad . \quad . \quad (43)$$

The above equations illustrate some of the statements made above. First, because the atoms are symmetrical only the r^{-2}, r^{-4}, and r^{-6} terms of these series are present, the odd powers being absent because their coefficients vanish. Secondly, if numerical values are assigned to b and to r, making $b=10^{-13}$ cm. and $r=10^{-8}$ cm., we have

$$\frac{b^6r^{-8}}{b^4r^{-6}} = \frac{b^4r^{-6}}{b^2r^{-4}} = b^2r^{-2} = 10^{-26+16} = 10^{-10}. \quad . \quad . \quad (44)$$

And since the coefficients involving Z, which is always unity or less, are negligible by comparison, it is evident that each succeeding term of these series is of the order 10^{10} times smaller than the preceding term. That is to say, the first term of each represents approximately the whole force.

While the force of any single electron in the second atom upon any one in the first obeys the inverse-square law, yet the effect of the whole second atom upon any one electron in the first obeys the inverse-fourth-power law, see (40) and (41), and the whole second atom on the first obeys the inverse-sixth-power law, see (42) and (43). Hence there are no inverse square forces acting within any atom of this type because of any distant neutral atom. By far the largest forces acting because of the second or distant atom are the inverse-fourth-power of the distant forces, and these have no effect upon the atom to produce any translational motion, but they set up an internal strain within the atom itself. The translational force upon the whole atom follows the inverse-sixth-power of the distance law, but these forces are minute as compared with those producing the internal strain as shown, since an r^{-6} term is nearly 10^{10} times smaller than an r^{-4} term.

As a result of this investigation it becomes evident that the larger energy transformations, taking place when molecules are formed from free atoms that were previously at a great distance apart, follow in the wake of the larger forces concerned, and are therefore manifested in the internal strain set up within the atom. Evidently this energy is traceable to a change in the energy content of the electrons themselves. But it is not profitable to pursue this simplified type of atom any further, because equations (42) and (43) show that there can be no equilibrium position where the two atoms will stand in stable equilibrium at any distance. Subsequent terms in the higher powers of r are of no value, and no values of the two variables Z and r will reduce both the x- and the z-components, that is the total force, to zero.

At first thought, without giving the matter full consideration, one might have imagined that no equilibrium for a system of point charges of this kind should be expected because of the general theorem of Ernshaw. This theorem, however, can have no bearing on this problem, for the reason that another condition has been imposed in that the two axes of the atoms have been assumed to be parallel to each other in all positions. This result is brought about by the rotation of each fundamental charge upon its own axis, which gives rise to an electromagnetic force that is not contemplated by Ernshaw's theorem. It is this rotation that keeps the two axes parallel, but after that we are merely concerned with the electrostatic forces, and these are all that we have to investigate for reasons that have been clearly stated in the previously published papers cited.

VI. *The Circle-and-Point-Electrons in a Symmetrical Atom.*

In the historical order the next form of atom subjected to computation approaches the form of fig. 1 much closer than the assumption of simple spheres as above. But this new computation still assumes a perfectly symmetrical atom, and makes no allowance for any internal strain, and on this account in the light of subsequent experience it could not be expected to be entirely successful and satisfactory. Because the solution of the problem of finding the electrostatic force exerted upon one oblate spheroid of the kind above described due to a second one on the assumption of the inverse-square law as between the infinitesimal elements of charge supposed to be uniformly distributed throughout the volume of the spheroid has never been obtained, it has been necessary to approach the condition of the model of fig. 1 by the use of solutions which are available.

In the closer approximation to the spheroid of the electron the inscribed sphere is imagined to be cut out. This leaves a ring of charge thickest at the equator and tapering in thickness towards the poles. The total charge of the electron is thus divided mentally into the sum of two—a sphere and a ring. The sphere may be represented mathematically by a point at its centre, and the ring may be approximated by considering it as the equivalent of a circle of the proper radius, whose centre coincides with the centre of the spheroid and whose plane is the equatorial plane. The oblate-spheroid-electron is thus replaced for mathematical requirements by a circle-and-point-electron. The approximation is close, however, and the eccentricity of the spheroid is represented in the circle-and-point-electron. A change in the eccentricity of the spheroid changes the size of the inscribed sphere, and because the charges are proportional to their volumes, some of the charge switches over from the point to the circle and *vice versa* in the circle-and-point-electron.

Denoting by ρ the ratio of the charge on the circle to the whole charge of the electron e, it is easy to show * that ρ is equal to the square of the eccentricity of the spheroid, so that

$$\rho = \epsilon^2. \qquad (45)$$

The charge on the point is then

$$E_1 = (1-\rho)e, \qquad (46)$$

and the charge on the circle is

$$E_2 = \rho e, \qquad (47)$$

their sum being

$$E_1 + E_2 = e. \qquad (48)$$

The ratio ρ, like ϵ, is always less than unity, and as the form of the spheroid changes from a sphere to a very flat spheroid more and more charge shifts over from the point to the circle. For the sphere both ρ and ϵ are zero, and $E_1 = e$, while $E_2 = 0$. As ρ approaches unity, E_1 approaches zero and E_2 approaches e.

The electrostatic force of one spheroid upon another is thus simplified to depend upon the force of one circle upon another. Fortunately this latter is obtainable. It may be found from the equation giving the average force * exerted by one point charge revolving in a circle upon another point charge revolving in a different circle. The equation assumes, however, that the planes of the two circles are parallel.

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* *Loc, cit.* second paper, p. 907.

VII. *The Electrostatic Force of a Second Stationary Circle of Charge upon a First Stationary Circle of Charge with Parallel Planes.*

Since this equation is fundamental to any solution involving circles, it will be given in full for reference. The force is that of a secondary stationary circle of radius a_2 uniformly charged around its circumference by a total charge of E_2 acting upon a first circle of radius a_1 with its circumference uniformly charged to the amount E_1, their planes being parallel to each other. For brevity the sum of the squares of the radii of the two circles is denoted by

$$\sigma = a_2^2 + a_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

and their product by

$$\delta = a_2 a_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

The three components of the force along the x-, y-, and z-axes are then as follows :—

$$\underset{\substack{\text{circle } a_2 \\ \text{on} \\ \text{circle } a_1}}{F_x} = \frac{E_1E_2}{k} X \Big[-r^{-2} + 3\sigma r^{-4} f_{x,4}(Z) - \tfrac{45}{8}(\sigma^2 + 2\delta^2) r^{-6} f_{x,6}(Z) \\ + \tfrac{35}{4}\sigma(\sigma^2 + 6\delta^2) r^{-8} f_{x,8}(Z) \\ - \tfrac{1575}{128}(\sigma^4 + 12\delta^2\sigma^2 + 6\delta^4) r^{-10} f_{x,10}(Z) \ldots \Big], \quad . \quad (51)$$

$$F_y = \frac{E_1E_2}{k} Y \,[\text{same bracket as in (51)}], \quad . \quad . \quad . \quad . \quad (52)$$

$$F_z = \frac{E_1E}{k} Z \Big[-r^{-2} + \tfrac{1}{2} \times 3\sigma r^{-4} f_{z,4}(Z) \\ - \tfrac{1}{3} \times \tfrac{45}{8}(\sigma^2 + 2\delta^2) r^{-6} f_{z,6}(Z) \\ + \tfrac{1}{4} \times \tfrac{35}{4}\sigma(\sigma^2 + 6\delta^2) r^{-8} f_{z,8}(Z) \\ - \tfrac{1}{5} \times \tfrac{1575}{128}(\sigma^4 + 12\delta^2\sigma^2 + 6\delta^4) r^{-10} f_{z,10}(Z) \ldots \Big], \\ . \quad . \quad . \quad . \quad (53)$$

---

* Crehore, Phil. Mag. July 1913, equations (42) and (44), pp. 69 and 70. The sign of (44) should be changed to minus, due to a misprint. In giving the numerical values of the constants B on p. 70, the first column should read $B_{4,2} = 5B_{2,2}$; $B_{6,2} = \frac{7}{2} B_{4,2}$; $B_{8,2} = \frac{9}{3} B_{6,2}$; $B_{10,2} = \frac{11}{4} B_{8,2}$; $B_{12,2} = \frac{13}{5} B_{10,2}$; $B_{14,2} = \frac{15}{6} B_{12,2}$. This correction was noted on p. 325, Phil. Mag. Feb. 1915, footnote.

where

$$
\begin{aligned}
f_{x,4}\,(\mathrm{Z}) &= a_4+b_4\mathrm{Z}^2, \\
f_{x,6}\,(\mathrm{Z}) &= a_6+b_6\,\mathrm{Z}^2+c_6\mathrm{Z}^4, \\
f_{x,8}\,(\mathrm{Z}) &= a_8+b_8\,\mathrm{Z}^2+c_8\mathrm{Z}^4+d_8\mathrm{Z}^6, \\
f_{x,10}(\mathrm{Z}) &= a_{10}+b_{10}\mathrm{Z}^2+c_{10}\mathrm{Z}^4+d_{10}\mathrm{Z}^6+e_{10}\mathrm{Z}^8\,; \quad . \quad . \quad . \quad (54)
\end{aligned}
$$

and

$$
\begin{aligned}
f_{z,4}\,(\mathrm{Z}) &= 6(a_4+\tfrac{1}{3}b_4\,\mathrm{Z}^2), \\
f_{z,6}\,(\mathrm{Z}) &= 15(a_6+\tfrac{1}{3}b_6\,\mathrm{Z}^2+\tfrac{1}{5}c_6\,\mathrm{Z}^4), \\
f_{z,8}\,(\mathrm{Z}) &= 28(a_8+\tfrac{1}{3}b_8\,\mathrm{Z}^2+\tfrac{1}{5}c_8\mathrm{Z}^4+\tfrac{1}{7}d_8\mathrm{Z}^6), \\
f_{z,10}(\mathrm{Z}) &= 45(a_{10}+\tfrac{1}{3}b_{10}\mathrm{Z}^2+\tfrac{1}{5}c_{10}\mathrm{Z}^4+\tfrac{1}{7}d_{10}\mathrm{Z}^6+\tfrac{1}{9}e_{10}\mathrm{Z}^8)\,; \quad . \quad (55)
\end{aligned}
$$

and where the numerics a, b, c, d, and e have the following values:

$$
\begin{array}{llll}
a_4=-\frac{1}{4}; & a_6=\frac{1}{8}; & a_8=-\frac{5}{64}; & a_{10}=\frac{7}{128}; \\
b_4=\frac{5}{4}; & b_6=-\frac{7}{4}; & b_8=\frac{135}{64}; & b_{10}=-\frac{77}{32}; \\
 & c_6=\frac{21}{8}; & c_8=-\frac{495}{64}; & c_{10}=\frac{1001}{64}; \\
 & & d_8=\frac{429}{64}; & d_{10}=-\frac{1001}{32}; \\
 & & & e_{10}=\frac{2431}{128}. \quad . \quad (56)
\end{array}
$$

The functions of Z given by (54) and (55) are not exactly the same as those given in (32) to (35), but they are multiples of them. The expression for the force has been developed to include the inverse tenth power of the distance r, but we shall not have occasion to make use of it for the purposes of this paper beyond the inverse sixth term. By means of this equation the total force of a second circle-and-point-electron acting upon a first such electron may be written down. The force of a circle upon a point charge may be obtained from this by making either radius a_2 or a_1 as the case may be equal to zero, and at the same time taking care that the proper charges are used for each body. The whole force of a second electron upon a first is thus the sum of four component parts—the force of the circle of the second on that of the first, the force of the point of the second on the circle of the first, the force of the circle of the second on the point of the first, and, lastly, the force of the point of the second upon the point of the first.

VIII. *The Electrostatic Force of a Second Circle-and-Point-Electron upon a First.*

Without giving each of these component parts above mentioned separately, the whole force of a second circle-and-point-electron of charge $-e$, radius a_2 and ratio of charge on the circle to the total charge, ρ_2, acting upon a first electron of the same charge but having different values of a and ρ denoted by a_1 and ρ_1, is as follows :—

$$\underset{\substack{\text{Second elec.}\\ \text{on a}\\ \text{First elec.}}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\big[-r^{-2}+\mathrm{A}r^{-4}f_{x,4}(\mathrm{Z})+\mathrm{B}r^{-6}f_{x,6}(\mathrm{Z})$$
$$+\mathrm{C}r^{-8}f_{x,8}(\mathrm{Z})+\mathrm{D}r^{-10}f_{x,10}(\mathrm{Z})\ldots\big], \quad . \quad (57)$$

$$\mathrm{F}_y = \frac{e^2}{\mathrm{k}}\mathrm{Y}\,[\text{same bracket as in (57)}], \quad . \quad . \quad . \quad . \quad (58)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\,\big[-r^{-2}+\tfrac{1}{2}\mathrm{A}r^{-4}f_{z,4}(\mathrm{Z})+\tfrac{1}{3}\mathrm{B}r^{-6}f_{z,6}(\mathrm{Z})$$
$$+\tfrac{1}{4}\mathrm{C}r^{-8}f_{z,8}(\mathrm{Z})+\tfrac{1}{5}\mathrm{D}r^{-10}f_{z,10}(\mathrm{Z})\ldots\big], \quad . \quad (59)$$

where

$$\mathrm{A}=3(\rho_2a_2^2+\rho_1a_1^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

$$\mathrm{B}=-\tfrac{45}{8}(4\rho_2\rho_1a_2^2a_1^2+\rho_2a_2^4+\rho_1a_1^4), \quad . \quad . \quad . \quad . \quad (61)$$

$$\mathrm{C}=\tfrac{35}{4}[9\rho_2\rho_1a_2^2a_1^2(a_2^2+a_1^2)+\rho_2a_2^6+\rho_1a_1^6], \quad . \quad . \quad (62)$$

$$\mathrm{D}=-\tfrac{1575}{128}(16\rho_2\rho_1a_2^2a_1^6+36\rho_2\rho_1a_2^4a_1^4$$
$$+16\rho_2\rho_1a_2^6a_1^2+\rho_2a_2^8+\rho_1a_1^8), \quad . \quad (63)$$

and where the functions of Z are the same as given in (54) and (55).

IX. *The Symmetrical Atom Form of Molecule.*

These fundamental equations may be used to obtain the force upon a first atom situated at the origin of coordinates due to a second atom in any general position (x, y) in a manner similar to the process employed above with spherical electrons. Only the results of these operations can be given here, but they have been carefully checked until we are assured of their accuracy upon the premises, namely their dependence upon their fundamental equations (57) to (59). These equations hold good for different kinds of electrons, those differing in a and ρ, but we shall now consider first the case where all electrons are alike and where the atom is a symmetrical structure, the centres of the three bodies A, B, and C being in one line, and the distances AC, BC, ac, and bc each equal to b, the semi-minor axis of the negative electron. Fig. 3 represents two such circle-and-point-electron atoms forming the molecule. The circles viewed on edge appear as lines.

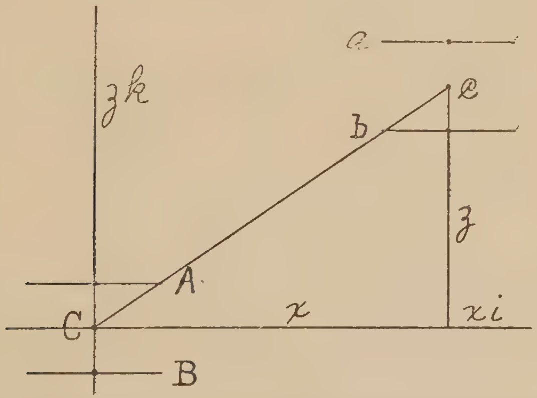
The force of the atom H_2 upon the positive charge alone, namely C, is as follows :—

$$\underset{\mathrm{H_2\ on\ C}}{F_x} = \frac{e^2}{k} X\Big[-6\left(b^2-\tfrac{1}{2}\rho a^2\right)r^{-4}f_{x,4}(Z) + \tfrac{15}{4}\left(2b^4-6b^2\rho a^2+\tfrac{3}{4}\rho a^4\right)r^{-6}f_{x,6}(Z)\ldots\Big], \qquad (64)$$

$$F_z = \frac{e^2}{k} Z\Big[-6\left(b^2-\tfrac{1}{2}\rho a^2\right)r^{-4}f_{z,4}(Z) + \tfrac{5}{4}\left(2b^4-6b^2\rho a^2+\tfrac{3}{4}\rho a^4\right)r^{-6}f_{z,6}(Z)\ldots\Big], \qquad (65)$$

where the functions of Z are as in (32) to (35).

Fig 3.



Hydrogen molecule with symmetrical atoms using circle-and-point electrons.

If ρ is put equal to zero in these expressions, it is equivalent to assuming that the electrons are spherical as before stated. When this is done (64) becomes identical with (30) and (65) with (31) after omitting the r^{-2} terms as before explained. So the result in these last equations is more general, including the former as a special case. The lowest order term, as before, is the r^{-4} term, and only even powers of r are present, because the atom is still assumed symmetrical and undeformed. The value of the force now, however, is completely altered, since it depends upon the relative values of b^2 and $\frac{1}{2}\rho a^2$. If these quantities were equal to each other the r^{-4} term would vanish entirely. Unless they are so closely equal that their difference is approximately 10^{10} times smaller than either term alone, then the r^{-4} term is far greater than the r^{-6} term, and it represents therefore the whole force. The numerical value of this quantity, which may be denoted by P, namely

$$P = b^2 - \tfrac{1}{2}\rho a^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

is

$$P = -1{\cdot}25 \times 10^{-26} \text{ cm.}^2. \quad . \quad . \quad . \quad (67)$$

In order not to interrupt the continuity of the presentation, the derivation of this numerical value for P is given in Appendix A to this paper. The second term of (66) is greater than the first, and the total greater than b^2 alone, but with the opposite sign. The value of b^2 alone is 10^{-26} cm.^{2} Hence the r^{-4} terms of (64) and (65) are by far the greatest.

The force upon the two electrons A and B together due to the second atom is given by

$$\underset{\substack{H_2 \text{ on} \\ A+B}}{F_r} = \frac{e^2}{k} X\left[6Pr^{-4} f_{x,4}(Z) - \tfrac{15}{4}(14b^4 - 18b^2\rho a^2 + 3\rho^2 a^4 \right.$$
$$\left. + \tfrac{3}{4}\rho a^4) r^{-6} f_{x,6}(Z) \ldots\right], \quad . \quad . \quad (68)$$

$$F_z = \frac{e^2}{k} Z\left[6Pr^{-4} f_{z,4}(Z) - \tfrac{5}{4}(14b^4 - 18b^2\rho a^2 + 3\rho^2 a^4 \right.$$
$$\left. + \tfrac{3}{4}\rho a^4) r^{-6} f_{z,6}(Z) \ldots\right], \quad . \quad . \quad (69)$$

and here also the r^{-4} terms are by far the largest of the series, but it is to be observed that the r^{-4} terms of the force on the two electrons in (68) or (69) are exactly equal and opposite to the r^{-4} terms respectively of the force upon the positive charge of (64) and (65). These large forces drop out when the sum is taken to obtain the force of the second atom upon the first which follows.

$$\underset{H_2 \text{ on } H_1}{F_x} = \frac{e^2}{k} X[-45P^2 r^{-6} f_{x,6}(Z) \ldots], \quad . \quad . \quad . \quad (70)$$

$$F_z = \frac{e^2}{k} Z[-15P^2 r^{-6} f_{z,6}(Z) \ldots], \quad . \quad . \quad . \quad (71)$$

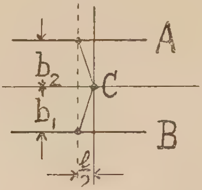
where P is given in (67), and the functions of Z in (34) and (35). This same equation developed to include the r^{-8} and r^{-10} terms is given as equation (17), p. 1029, Phil. Mag. for June 1922. An attempt was made in that paper to obtain an equilibrium by means of this symmetrical atom, using the r^{-6}, r^{-8}, and r^{-10} terms and taking P as an unknown quantity to which different numerical values might be assigned. In the r^{-6} term the square of P occurs as a factor, while in the r^{-8} term the first power of P is a factor, and in the r^{-10} term it is not a factor. But to obtain any equilibrium a value of P must be chosen such as to render the magnitudes of the three terms of the same order. Such a value was found in the neighbourhood of 7×10^{-35} for P, which requires that the two terms of (66) shall be equal to each other to a very exact degree. This in itself seems improbable. Moreover, the forces with such a small value for P are much too small, each term being of the order $\frac{e^2}{\mathrm{k}}10^{-22}$ dyne near the position of equilibrium. And again, the law of force between the atoms of a solid body would then appear to be higher than the inverse-sixth power of the distance, which is not supported by experimental evidence. Such evidence indicates that the variation of the force with the distance obeys the inverse-fifth power of the distance law nearer than any other.

On the other hand the symmetrical and undeformed atom of fig. 2 with spheres offers no possibility of forming a molecule with two such atoms at a distance of the order of 10^{-8} cm., while the atom of fig. 3 with circle-and-point-electrons shows that such a thing is quite possible, and this in itself seemed an important result. But a further study of the problem has shown that the former attempt to obtain an equilibrium in the paper referred to is open to the objection above mentioned, and these objections have all been removed by the subsequent development. The part played by the comparatively large forces expressed by the r^{-4} terms in (68) and (69) cannot be neglected, because the energy changes that take place as the molecule is being formed are necessarily connected with these larger forces; but these are manifested only within the atom itself, and produce an internal strain. When these strains are taken into the account the problem becomes much enlarged in scope and more complex, but if this is the truth of the matter the situation must be faced.

X. *The Unsymmetrical and Deformed Atom.*

The effect of the x-component of the force of the second atom upon the positive charge and upon the two electrons of the first atom is to pull the one to the right and the other to the left, thus very slightly displacing the positive charge off from the line joining the centres of the two electrons, as illustrated in fig. 4. The sum of these displacements in the two atoms of a molecule may be denoted by l, while $l/2$ denotes that in the single atom of fig. 4. The magnitude of the displacement will be shown to be less than the radius of the positive charge itself, and in order to show it in the figure it has been greatly magnified. Circle-and-point-electrons are illustrated in the figure, but it should be kept in mind that the electrons are oblate spheroids in contact with the positive charge.

Fig. 4.

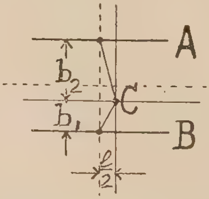


Hydrogen atom with circle-and-point electrons illustrating the x-displacement.

The effect of the z-component of the force is to increase the pressure between an electron, say B, and the positive charge, and to lessen the pressure between the other electron, A, and the positive charge. This increases the area of the one electron, B, and reduces slightly its minor axis, and decreases the area of A, increasing its minor axis, but not necessarily by the same amount as that of B was increased, since the force of the second atom upon A differs slightly from that upon B on account of their different distances.

Fig. 5 represents the effect of the z-component of the force upon H_1 together with that of the x-component. The vertical distance from A to C has increased from b in fig. 3 to b_2 in fig. 5, while that from B to C has diminished from b to b_1. It is conceivable that the minor axis of A increases by just the same amount as that of B decreases, in which

Fig. 5.



Hydrogen atom illustrating both the x- and z-displacements.

case the vertical distance from A to B would remain unchanged. But when the axis of A increases, this electron performs work giving up some of its energy content, and similarly, when the axis of B decreases, work must be done upon it to increase its surface, and it consequently absorbs energy. If the amounts of the increase of the axis of A and the decrease of that of B were the same, then all of the energy given up by A would be reabsorbed by B, and there would occur no total change in the energy content of the atom. As long, therefore, as the vertical distance from the centre of A to that of B remains the same as it was in the free atom, so long does the energy of the whole atom remain unchanged. But if the distance AB increases over and above its value in the free atom, then work has been done by the atoms in forming the molecule at the expense of some of the energy content of the electrons as they existed in the free atoms. Since it is true that work must be done by outside influences to separate the molecule of hydrogen into free atoms and thus restore the two electrons of an atom to the condition they have in free atoms, it may be concluded that the distance AB must be slightly greater when the atom forms part of a molecule than when the atom is free. This means also that the over-all axial distance from the top surface of A to the bottom surface of B in fig. 1 must be slightly greater in the molecule than in the free atom.

XI. *The Energy of Dissociation of the Hydrogen Molecule.*

Let it be supposed, therefore, that the semi-minor axis of A increases from b to b_2 and that of B decreases from b to b_1, so that the change in that of A is b_2-b and in that of B, b_1-b; then, according to (26) above, the change in their respective energy contents is:

$$\text{For A,} \quad \Delta E_A = -6{\cdot}964\times10^6(b_2-b), \quad . \quad . \quad . \quad (72)$$

$$\text{and for B,} \quad \Delta E_B = -6{\cdot}964\times10^6(b_1-b). \quad . \quad . \quad . \quad (73)$$

The sum of these two energies represents the work done by the atom in forming the molecule, and is

$$\Delta E_A + \Delta E_B = -6{\cdot}964\times10^6[(b_2+b_1)-2b], \quad . \quad (74)$$

which must be negative as representing a loss of energy content on the whole. Now $2(b_2+b_1)$ is the polar diameter of the atom when in the molecule, and $4b$ its diameter when free; so that it is evident that the new diameter must be greater than the free diameter. This neglects the very small diameter of the positive charge of the order of 10^{-16} cm., which cancels any way in subtracting.

The new semi-minor axis of A may then be expressed as

$$b_2 = b+a+h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

and of B,

$$b_1 = b-a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

where a now represents the major part of the change in the semi-minor axis as the molecule is formed, and h represents the very small excess of change of electron A over that of B. From this we find that

$$b_2-b_1 = 2a+h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (77)$$

$$\text{and} \quad b_2+b_1 = 2b+h,$$

$$\text{or} \quad h = (b_2+b_1)-2b \, ; \quad . \quad . \quad . \quad (78)$$

and so by (74) h is not only proportional to the whole work done in forming the molecule, but it also represents half the difference between the new and old polar diameters of the atom.

Using the experimental value of the energy of dissociation of the hydrogen molecule (Langmuir) as $5{\cdot}8\times10^{-12}$ erg, and one-half of this as the energy change per atom, we have from (74)

$$\Delta E = -\frac{5{\cdot}8}{2}10^{-12} = \Delta E_A + \Delta E_B = -6{\cdot}964\times10^{6}h, \quad (79)$$

whence the value of h becomes known numerically as

$$h = \frac{5{\cdot}8}{2\times6{\cdot}964}10^{-18} = \frac{58}{13{\cdot}928}10^{-19} = 4{\cdot}164\times10^{-19}\text{ cm.} \quad . \quad . \quad . \quad (80)$$

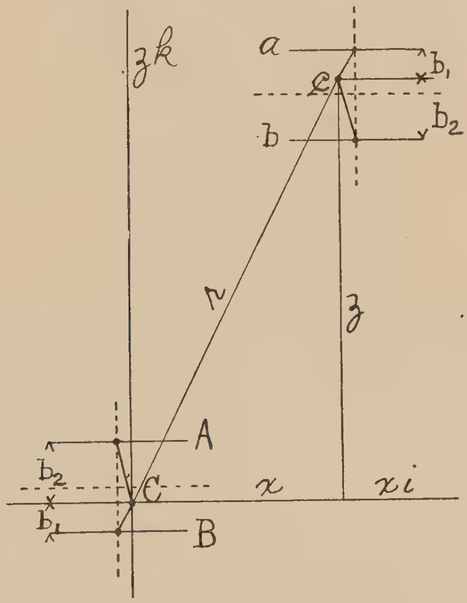
This is its value at the point of equilibrium of the two atoms when in the molecule, and is about 1/240,000th part of the semi-minor axis of the electron itself. The principal change in the minor axis is, however, greater than h; that is to say, the a of (75) and (76) is considerably larger than h.

XII. *The Forces acting upon the Individual Bodies of the First Atom of the Deformed Molecule.*

The complication that arises when allowance is made for the internal stresses within the atom itself as the molecule is formed is due to the circumstance that there is no longer a fixed atom that may be moved about from place to place, as there was in the cases above considered and illustrated by figs. 2 and 3, but the atom itself now changes with each new position. Instead of having but two variables to manage as in (70) and (71) above, the Z and the r, there are now five variables, namely Z, r, l, b_2, and b_1, all of which change with the relative positions of the atoms.

The resulting equations obtained with two such variable atoms, such as represented in fig. 5, and also shown as a molecule in fig. 6, will now be given in full without the rather laborious detail of their derivation. The principles of the operations as depending only upon electrostatic forces in the circle-and-point-electron approximation to the oblate spheroid have been fully explained above, and the work has been carefully checked, so that it is believed that the resulting equations are trustworthy as depending upon these premises.

Fig. 6.



The hydrogen molecule with deformed or strained atoms.

The force upon the positive charge, C, of the atom H_1 due to the two electrons only, a and b of the second atom, is given in (81) and (92) for the x- and the z-components of the force respectively up to and including the r^{-6} term. The force of the whole atom, H_2, upon C is found from this by adding the force of the positive charge, c upon C, which comes to the same thing as omitting the r^{-2} terms from (81) and (92), and hence this need not be written down again. The same thing occurred before in discussing equations (30) and (31) in the simpler case of the spherical electrons.

The equations that follow are complete, including the r^{-6} term, no terms having been omitted in the development, and are given for reference, although it will appear subsequently that they may be greatly simplified by omitting certain terms as unimportant when numerical values are introduced.

$$\begin{aligned}
\underset{a+b \text{ on C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\Big\{ & 4\mathrm{X}r^{-2} - 2[(2-3\mathrm{Z}^2)l - 3\mathrm{XZD}]r^{-3} \\
& + \Big[\tfrac{3}{2}(2-5\mathrm{Z}^2)\mathrm{X}l^2 - 3(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\
& \quad - 3(1-5\mathrm{Z}^2)\mathrm{X}[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2a_2^2+\rho_1a_1^2)]\Big]r^{-4} \\
& + \Big[-\tfrac{1}{4}l^3 f_0(\mathrm{Z}) + \tfrac{15}{4}l^2\mathrm{D}\,f_1(\mathrm{Z}) \\
& \quad + \tfrac{3}{2}l[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2a_2^2+\rho_1a_1^2)]\,f_2(\mathrm{Z}) \\
& \quad - 5[(b_2^3-b_1^3) - \tfrac{3}{2}(b_2\rho_2a_2^2 - b_1\rho_1a_1^2)]\,f_3(\mathrm{Z})\Big]r^{-5} \\
& + \Big[\tfrac{5}{4}\mathrm{X}l^4 f_4(\mathrm{Z}) - \tfrac{15}{8}\mathrm{Z}l^3\mathrm{D}\,f_5(\mathrm{Z}) \\
& \quad - \tfrac{15}{8}\mathrm{X}l^2[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2a_2^2+\rho_1a_1^2)]\,f_6(\mathrm{Z}) \\
& \quad + \tfrac{5}{2}\mathrm{Z}l[(b_2^3-b_1^3) - \tfrac{3}{2}(b_2\rho_2a_2^2 - b_1\rho_1a_1^2)]\,f_7(\mathrm{Z}) \\
& \quad + \tfrac{15}{4}\mathrm{X}[(b_2^4+b_1^4) - 3(b_2^2\rho_2a_2^2 + b_1^2\rho_1a_1^2) \\
& \quad + \tfrac{3}{8}(\rho_2a_2^4+\rho_1a_1^4)]\,f_8(\mathrm{Z})\Big]r^{-6} \ldots\Big\}, \quad . \quad . \quad (81)
\end{aligned}$$

where

$$f_0(\mathrm{Z}) = 8-40\mathrm{Z}^2+35\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (82)$$

$$f_1(\mathrm{Z}) = (4-7\mathrm{Z}^2)\mathrm{XZ}, \quad . \quad . \quad . \quad . \quad . \quad (83)$$

$$f_2(\mathrm{Z}) = 4-35\mathrm{Z}^2+35\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (84)$$

$$f_3(\mathrm{Z}) = (3-7\mathrm{Z}^2)\mathrm{XZ}, \quad . \quad . \quad . \quad . \quad . \quad (85)$$

$$f_4(\mathrm{Z}) = 1-7\mathrm{Z}^2+\tfrac{63}{8}\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (86)$$

$$f_5(\mathrm{Z}) = 8-28\mathrm{Z}^2+21\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (87)$$

$$f_6(\mathrm{Z}) = 4-49\mathrm{Z}^2+63\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (88)$$

$$f_7(\mathrm{Z}) = 18-77\mathrm{Z}^2+63\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (89)$$

$$f_8(\mathrm{Z}) = 1-14\mathrm{Z}^2+21\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (90)$$

and $\mathrm{D} = b_2-b_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$

$$\begin{aligned}
\underset{a+b\text{ on C}}{F_z} = \frac{\epsilon^2}{k}\{ & 4Zr^{-2} - 2[3XZl + (1-3Z^2)D]r^{-3} \\
& + [\tfrac{3}{2}(4-5Z^2)Zl^2 + 3(1-5Z^2)XlD \\
& \quad - 3(3-5Z^2)Z[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)]]r^{-4} \\
& + [-\tfrac{5}{4}l^3 f_1(Z) - \tfrac{3}{4}l^2 D f_2(Z) \\
& \quad + \tfrac{15}{2}l[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)] f_3(Z) \\
& \quad + [(b_2^3-b_1^3) - \tfrac{3}{2}(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2)] f_9(Z)]r^{-5} \\
& + [\tfrac{15}{32}l^4 Z f_5(Z) + \tfrac{5}{8}l^3 DX f_6(Z) \\
& \quad - \tfrac{15}{8}l^2 Z[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)] f_7(Z) \\
& \quad - \tfrac{15}{2}lX[(b_2^3-b_1^3) - \tfrac{3}{2}(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2)] f_8(Z) \\
& \quad + \tfrac{5}{4}Z[(b_2^4+b_1^4) - 3(b_2^2\rho_2 a_2^2 + b_1^2\rho_1 a_1^2) \\
& \quad + \tfrac{3}{8}(\rho_2 a_2^4 + \rho_1 a_1^4)] f_{10}(Z)]r^{-6}\ldots\ldots\}, \qquad . \quad (92)
\end{aligned}$$

where

$$f_9(Z) = 3 - 30Z^2 + 35Z^4 \quad . \quad . \quad . \quad . \quad (93)$$

and

$$f_{10}(Z) = 15 - 70Z^2 + 63Z^4, \quad . \quad . \quad . \quad . \quad (94)$$

the other functions of Z being as given in (82) to (90).

The force upon the two electrons A and B together of the first atom due to the two electrons *a* and *b* together of the second atom is given by (95) and (96), which follow.

$$\begin{aligned}
\underset{\substack{a+b\text{ on}\\ A+B}}{F_x} = \frac{\epsilon^2}{k}\{ & -4Xr^{-2} + 4[(2-3Z^2)l - 3XZD]r^{-3} \\
& + [-6(2-5Z^2)Xl^2 + 12(4-5Z^2)ZlD \\
& \quad + 3(1-5Z^2)X[2(b_2^2+b_1^2) - (\rho_2 a_2^2 + \rho_1 a_1^2) + D^2]]r^{-4} \\
& + [2l^3 f_0(Z) - 30l^2 D f_1(Z) - 3l[2(b_2^2+b_1^2) \\
& \quad - (\rho_2 a_2^2 + \rho_1 a_1^2) + D^2] f_2(Z) + 5[D^3 + 4(b_2^3-b_1^3) \\
& \quad - 3(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2) - \tfrac{3}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)D] f_3(Z)]r^{-5} \\
& + [-20Xl^4 f_4(Z) + 30Zl^3 D f_5(Z) \\
& \quad + \tfrac{15}{2}Xl^2[D^2 + 2(b_2^2+b_1^2) - (\rho_2 a_2^2 + \rho_1 a_1^2)] f_6(Z) \\
& \quad - 5Zl[D^3 + 4(b_2^3-b_1^3) - 3(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2) \\
& \quad - \tfrac{3}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)D] f_7(Z) \\
& \quad - \tfrac{15}{4}X[D^4 + 8(b_2^4+b_1^4) + \tfrac{3}{4}(\rho_2 a_2^2 + \rho_1 a_1^2)^2 \\
& \quad + \tfrac{3}{4}(\rho_2 a_2^4 + \rho_1 a_1^4) - 3(\rho_2 a_2^2 + \rho_1 a_1^2)D^2 \\
& \quad - 12(b_2^2\rho_2 a_2^2 + b_1^2\rho_1 a_1^2)] f_8(Z)]r^{-6}\ldots\}. \qquad . \quad . \quad (95)
\end{aligned}$$

$$
\begin{aligned}
\underset{\substack{a+b \text{ on}\\ \mathrm{A+B}}}{\mathrm{F}_z} = \frac{e^2}{\mathrm{k}} \Big\{ & -4\mathrm{Z}r^{-2}+4[3\mathrm{XZ}l+(1-3\mathrm{Z}^2)\mathrm{D}]r^{-3} \\
& +\big[-6(4-5\mathrm{Z}^2)\mathrm{Z}l^2-12(1-5\mathrm{Z}^2)\mathrm{X}l\mathrm{D} \\
& \quad +3(3-5\mathrm{Z}^2)\mathrm{Z}[2(b_2{}^2+b_1{}^2)-(\rho_2a_2{}^2+\rho_1a_1{}^2)+\mathrm{D}^2]\big]r^{-4} \\
& +\big[10l^3f_1(\mathrm{Z})+6l^2\mathrm{D}f_2(\mathrm{Z})-15l[2(b_2{}^2+b_1{}^2) \\
& \quad -(\rho_2a_2{}^2+\rho_1a_1{}^2)+\mathrm{D}^2]f_3(\mathrm{Z})-[\mathrm{D}^3+4(b_2{}^3-b_1{}^3) \\
& \quad -3(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2)-\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_9(\mathrm{Z})\big]r^{-5} \\
& +\big[-\tfrac{15}{2}\mathrm{Z}l^4f_5(\mathrm{Z})-10\mathrm{X}l^3\mathrm{D}f_6(\mathrm{Z}) \\
& \quad +\tfrac{15}{2}\mathrm{Z}l^2[\mathrm{D}^2+2(b_2{}^2+b_1{}^2)-(\rho_2a_2{}^2+\rho_1a_1{}^2)]f_7(\mathrm{Z}) \\
& \quad +15\mathrm{X}l[\mathrm{D}^3+4(b_2{}^3-b_1{}^3)-3(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2) \\
& \quad -\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_8(\mathrm{Z}) \\
& \quad -\tfrac{5}{4}\mathrm{Z}[\mathrm{D}^4+8(b_2{}^4+b_1{}^4)+\tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2 \\
& \quad +\tfrac{3}{4}(\rho_2a_2{}^4+\rho_1a_1{}^4)-3(\rho^2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad -12(b_2{}^2\rho_2a_2{}^2+b_1{}^2\rho_1a_1{}^2)]f_{10}(\mathrm{Z})\big]r^{-6}\ldots\Big\}, \quad . \quad . \quad (96)
\end{aligned}
$$

where the functions of Z are given by (82) to (94) above.

The force of the whole atom, H_2, upon the two electrons A and B together of the first atom is merely the sum of (81) and (95) for the x-component, and of (92) and (96) for the z-component, because the force of the positive charge, c, upon A and B together is exactly the same as that of a and b together upon the positive charge C. These sums are given by (97) and (98), which follow.

$$
\begin{aligned}
\underset{\substack{\mathrm{H}_2 \text{ on}\\ \mathrm{A+B}}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}} \Big\{ & 2[(2-3\mathrm{Z}^2)l-3\mathrm{XZD}]r^{-3} \\
& +\big[-\tfrac{9}{2}(2-5\mathrm{Z}^2)\mathrm{X}l^2+9(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\
& \quad +3(1-5\mathrm{Z}^2)\mathrm{X}[(b_2{}^2+b_1{}^2)-\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\mathrm{D}^2]\big]r^{-4} \\
& +\big[\tfrac{7}{4}l^3f_0(\mathrm{Z})-\tfrac{105}{4}l^2\mathrm{D}f_1(\mathrm{Z})-\tfrac{9}{2}l[(b_2{}^2+b_1{}^2) \\
& \quad -\tfrac{1}{2}((\rho_2a_2{}^2+\rho_1a_1{}^2)+\tfrac{2}{3}\mathrm{D}^2]f_2(\mathrm{Z})+5[\mathrm{D}^3+3(b_2{}^3-b_1{}^3) \\
& \quad -\tfrac{3}{2}(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2)-\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_3(\mathrm{Z})\big]r^{-5} \\
& +\big[-\tfrac{75}{4}\mathrm{X}l^4f_4(\mathrm{Z})+\tfrac{225}{8}\mathrm{Z}l^3\mathrm{D}f_5(\mathrm{Z})+\tfrac{105}{8}\mathrm{X}l^2[(b_2{}^2+b_1{}^2) \\
& \quad -\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\tfrac{4}{7}\mathrm{D}^2]f_6(\mathrm{Z})-5\mathrm{Z}l[\mathrm{D}^3+\tfrac{7}{2}(b_2{}^3-b_1{}^3) \\
& \quad -\tfrac{9}{4}(b_2\rho_2a_2{}^2-b_1a_1\rho_1{}^2)-\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_7(\mathrm{Z}) \\
& \quad -\tfrac{15}{4}\mathrm{X}[\mathrm{D}^4+7(b_2{}^4+b_1{}^4)+\tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2 \\
& \quad +\tfrac{3}{8}(\rho_2a_2{}^4+\rho_1a_1{}^4)-3(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad -9(b_2{}^2\rho_2a_2{}^2+b_1{}^2\rho_1a_1{}^2)]f_8(\mathrm{Z})\big]r^{-6}\ldots\Big\}. \quad . \quad . \quad . \quad (97)
\end{aligned}
$$

$$
\begin{aligned}
\underset{\substack{\mathrm{H_2\ on}\\ \mathrm{A+B}}}{\mathrm{F}_z} = \frac{e^2}{\mathrm{k}}\{ & 2[3\mathrm{XZ}l+(1-3\mathrm{Z}^2)\mathrm{D}]r^{-3} \\
& +[-\tfrac{9}{2}(4-5\mathrm{Z}^2)\mathrm{Z}l^2-9(1-5\mathrm{Z}^2)\mathrm{X}l\mathrm{D} \\
& \quad +3(3-5\mathrm{Z}^2)\mathrm{Z}[(b_2{}^2+b_1{}^2)-\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\mathrm{D}^2]]r^{-4} \\
& +[\tfrac{35}{4}l^3f_1(\mathrm{Z})+\tfrac{21}{4}l^2\mathrm{D}f_2(\mathrm{Z})-\tfrac{45}{2}l[(b_2{}^2+b_1{}^2) \\
& \quad -\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\tfrac{2}{3}\mathrm{D}^2]f_3(\mathrm{Z})-[\mathrm{D}^3+3(b_2{}^3-b_1{}^3) \\
& \quad -\tfrac{3}{2}(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2)-\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_9(\mathrm{Z})]r^{-5} \\
& +[-\tfrac{225}{32}\mathrm{Z}l^4f_5(\mathrm{Z})-\tfrac{75}{8}\mathrm{X}l^3\mathrm{D}f_6(\mathrm{Z}) \\
& \quad +\tfrac{105}{8}\mathrm{Z}l^2[(b_2{}^2+b_1{}^2)-\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\tfrac{4}{7}\mathrm{D}^2]f_7(\mathrm{Z}) \\
& \quad +15\mathrm{X}l[\mathrm{D}^3+\tfrac{7}{2}(b_2{}^3-b_1{}^3)-\tfrac{9}{4}(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2) \\
& \quad -\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_8(\mathrm{Z})-\tfrac{5}{4}\mathrm{Z}[\mathrm{D}^4+7(b_2{}^4+b_1{}^4) \\
& \quad +\tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2+\tfrac{3}{8}(\rho_2a_2{}^4+\rho_1a_1{}^4) \\
& \quad -3(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad -9(b_2{}^2\rho_2a_2{}^2+b_1{}^2\rho_1a_1{}^2)]f_{10}(\mathrm{Z})]r^{-6}\ldots\}. \qquad (98)
\end{aligned}
$$

And finally the force upon the whole atom, H_1, due to the second atom, H_2, is found by adding (81) without the r^{-2} term to (97) for the x-component, and adding (92) without its r^{-2} term to (98) for the z-component, giving (99) and (100), which follow.

$$
\begin{aligned}
\underset{\mathrm{H_2 on H_1}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\{ & [-3(2-5\mathrm{Z}^2)\mathrm{X}l^2+6(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\
& \quad +3(1-5\mathrm{Z}^2)\mathrm{X}\mathrm{D}^2]r^{-4} \\
& +[\tfrac{3}{2}l^3f_0(\mathrm{Z})-\tfrac{45}{2}l^2\mathrm{D}f_1(\mathrm{Z})-3l[(b_2{}^2+b_1{}^2) \\
& \quad -\tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)+\mathrm{D}^2]f_2(\mathrm{Z})+5[\mathrm{D}^3+2(b_2{}^3-b_1{}^3) \\
& \quad -\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_3(\mathrm{Z})]r^{-5} \\
& +[-\tfrac{35}{2}\mathrm{X}l^4f_4(\mathrm{Z})+\tfrac{105}{4}\mathrm{Z}l^3\mathrm{D}f_5(\mathrm{Z}) \\
& \quad +\tfrac{15}{2}\mathrm{X}l^2[\mathrm{D}^2+\tfrac{3}{2}(b_2{}^2+b_1{}^2)-\tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)]f_6(\mathrm{Z}) \\
& \quad -5\mathrm{Z}l[\mathrm{D}^3+3(b_2{}^3-b_1{}^3)-\tfrac{3}{2}(b_2\rho_2a_2{}^2-b_1\rho_1a_1{}^2) \\
& \quad -\tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}]f_7(\mathrm{Z})-\tfrac{15}{4}\mathrm{X}[\mathrm{D}^4+6(b_2{}^4+b_1{}^4) \\
& \quad +\tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2-3(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad -6(b_2{}^2\rho_2a_2{}^2+b_1{}^2\rho_1a_1{}^2)]f_8(\mathrm{Z})]r^{-6}\ldots\}. \qquad (99)
\end{aligned}
$$

$$
\begin{aligned}
\underset{\mathrm{H}_2 \text{ on } \mathrm{H}_1}{\mathrm{F}_z} = \frac{e^2}{\mathrm{k}} \{ & [-3(4-5\mathrm{Z}^2)\mathrm{Z}l^2 \\
& -6(1-5\mathrm{Z}^2)\mathrm{X}l\mathrm{D}+3(3-5\mathrm{Z}^2)\mathrm{Z}\mathrm{D}^2]r^{-4} \\
& +[\tfrac{15}{2}l^3 f_1(\mathrm{Z})+\tfrac{9}{2}l^2\mathrm{D}f_2(\mathrm{Z})-15l[(b_2{}^2+b_1{}^2) \\
& -\tfrac{1}{2}(\rho_2 a_2{}^2+\rho_1 a_1{}^2)+\mathrm{D}^2]f_3(\mathrm{Z})-[\mathrm{D}^3+2(b_2{}^3-b_1{}^3) \\
& -\tfrac{3}{2}(\rho_2 a_2{}^2+\rho_1 a_1{}^2)\mathrm{D}]f_9(\mathrm{Z})]r^{-5} \\
& +[-\tfrac{45}{2}\mathrm{Z}l^4 f_5(\mathrm{Z})-\tfrac{35}{4}\mathrm{X}l^3\mathrm{D}f_6(\mathrm{Z}) \\
& +\tfrac{15}{4}\mathrm{Z}l^2[\mathrm{D}^2+2(b_2{}^2+b_1{}^2)-(\rho_2 a_2{}^2+\rho_1 a_1{}^2)]f_7(\mathrm{Z}) \\
& +15\mathrm{X}l[\mathrm{D}^3+3(b_2{}^3-b_1{}^3)+\tfrac{3}{2}(b_2\rho_2 a_2{}^2-b_1\rho_1 a_1{}^2) \\
& -\tfrac{3}{2}(\rho_2 a_2{}^2+\rho_1 a_1{}^2)\mathrm{D}]f_8(\mathrm{Z})-\tfrac{5}{4}\mathrm{Z}[\mathrm{D}^4+6(b_2{}^4+b_1{}^4) \\
& +\tfrac{3}{4}(\rho_2 a_2{}^2+\rho_1 a_1{}^2)^2-3(\rho_2 a_2{}^2+\rho_1 a_1{}^2)\mathrm{D}^2 \\
& -6(b_2{}^2\rho_2 a_2{}^2+b_1{}^2\rho_1 a_1{}^2)]f_{10}(\mathrm{Z})]r^{-6}\ldots\}, \quad . \quad (100)
\end{aligned}
$$

where the functions of Z are given by (82) to (94).

These equations reduce immediately to those for the symmetrical fixed atoms of fig. 3, (70) and (71), if the four electrons are made alike by putting $b_2=b_1$, $\rho_2=\rho_1$, and $a_2=a_1$, and if the atoms are made symmetrical by making $l=0$. In doing this both the r^{-4} and the r^{-5} terms disappear, so that the series, which begins with the r^{-4} term for the strained atom, begins with the r^{-6} for the symmetrical atom.

In the expressions for the force of H_2 on C, (81) and (92) without their r^{-2} terms, the odd power terms in r^{-3} and r^{-5} are present, whereas they are absent from the corresponding expressions for the symmetrical atoms in (64) and (65).

Another striking point of difference between these and the simpler equations is that the direction cosines, X and Z, are no longer factors of the whole force as they formerly were. We may now proceed to simplify some of the expressions by giving attention to the numerical values of the quantities concerned.

XIII. *The Introduction of Numerical Values in the above Equations.*

In the first place it is clear that both quantities, l and $\mathrm{D}=b_2-b_1$, must be far smaller than b, for b_2 must have very nearly the same value as b_1. It has already been shown in (78) and (80) that

$$h = (b_2+b_1)-2b = \cdot 4164\times 10^{-18} \text{ cm.}, \quad . \quad (101)$$

so that when the sum of the radii is concerned it differs by only about $\cdot 4 \times 10^{-18}$ cm. from $2b$, which difference is negligible by comparison with b. The same statement also applies to the quantity $(\rho_2 a_2^2 + \rho_1 a_1^2)$, which is closely equal to $2\rho a^2$. Hence the quantity,

$$(b_2^2 + b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2),$$

which occurs in the equations may without sensible error be replaced by

$$2(b^2 - \tfrac{1}{2}\rho a^2) = 2\mathrm{P},$$

where P is given by (67) above.

The largest forces concerned are those internal forces producing a strain within the atom, of which (81) and (92) without their r^{-2} terms represent the force upon the positive charge alone due to the second atom. In the position of stable equilibrium this force on the positive charge is exactly counterbalanced by the opposite forces upon the two negative electrons. The largest terms of this force are the r^{-3} and r^{-4} terms, the higher powers becoming rapidly small. For example, the largest part of the r^{-5} term of (81) is of the order $l\mathrm{P}r^{-5}$ as compared with the largest part of the r^{-4} term $\mathrm{P}r^{-4}$, or numerically, taking r in round numbers as 10^{-8} cm., the r^{-5} and r^{-4} terms compare as $l \times 10^{14}$ to 10^6. But l is of necessity far less than b in order that the atom remains intact, and in fact comes out of the order of 10^{-18} cm. Hence the r^{-5} and all following terms of (81) and (92) are negligible, and may be omitted without sensible error. Making these simplifications reduces (81) to the following simpler form:

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\{-2[(2-3\mathrm{Z}^2)l - 3\mathrm{XZD}]r^{-3} \\ -6(1-5\mathrm{Z}^2)\mathrm{XP}r^{-4}\ldots\}, \quad . \quad (102)$$

and (92) to the following:

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\{-2[3\mathrm{XZ}l + (1-3\mathrm{Z}^2)\mathrm{D}]r^{-3} \\ -6(3-5\mathrm{Z}^2)\mathrm{ZP}r^{-4}\ldots\}, \quad . \quad (103)$$

The whole of the r^{-3} terms have been retained, but the r^{-4} terms have been simplified by omitting the l^2 and the $l\mathrm{D}$ parts because they are very small as compared with P.

XIV. *The Value of the Displacement "l."*

The x-component of the force of the second atom upon the positive charge, C, produces the strain in the atom represented by the small displacement, $l/2$, of figs. 4, 5, and 6. It is legitimate to take this displacement as proportional to the force producing it for very small displacements such as those contemplated. The force (102) may therefore be set equal to the displacement multiplied by some constant, say $\frac{e^2}{k}\rho_x$, which is strictly characteristic of this form of atom. Since the displacement in one atom is $l/2$, we obtain

$$\underset{H_2 \text{ on } C}{F_x} = \frac{e^2}{k}\rho_x\frac{l}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (104)$$

The numerical value of this constant is unknown at present. A computation of its value might be made independently if we possessed the complete expression for the force of one oblate spheroid of charge acting upon another which is not yet known. It is evident that the approximate form for the electron used above, called the circle-and-point-electron, will not answer for such a purpose where the charges are so close as to be in contact with each other.

Upon equating (102) and (104) the $\frac{e^2}{k}$ cancels, giving

$$-2(2-3Z^2)lr^{-3}+6XZDr^{-3}-6(1-5Z^2)XPr^{-4}=\rho_x\frac{l}{2}, \quad (105)$$

which may easily be solved for l, giving

$$l=\frac{3XZDr^{-3}-3(1-5Z^2)XPr^{-4}}{(2-3Z^2)r^{-3}+\rho_x/4}. \quad . \quad . \quad . \quad (106)$$

Similarly the z-component of the force upon C produces the strain within the atom which is represented by the small change in the semi-minor axes of the two electrons, the quantity $D=b_2-b_1$ occurring in the equations. There is produced by it a change in the pressure between each electron and the positive charge. In the free state of the atoms b_2 and b_1 are equal to each other, their difference being zero; but as the molecule is formed, this difference changes gradually from zero to D, the forces upon the two electrons A and B being responsible for this change. For very small changes such as here contemplated it is legitimate to take D as proportional to the z-component of the force upon the positive charge, C, which is equal and opposite to the forces upon the two electrons in the position of equilibrium. Hence we may put

$$\underset{H_2 \text{ on } C}{F_z} = -\frac{e^2}{k}\rho_z D, \quad . \quad . \quad . \quad . \quad . \quad (107)$$

where ρ_z is some constant. That the negative sign is necessary here is apparent as follows:—If the z-component of the force upon C is positive, it acts in the upward direction in fig. 6, and must contract the upper electron A and expand the lower electron B. Hence b_2, which denotes the semi-minor axis for A, must be less than b_1, which denotes that of B. This would make b_2-b_1 negative when F_z is positive. The negative sign in (107) always makes F_z take the opposite sign to D, assuming that ρ_z is essentially positive, so that in the case just cited the force is positive. On the other hand, when F_z is negative and downward in fig. 6, then b_2 is greater than b_1 and D is positive, so that the negative sign is correct in either case.

Upon equating this new expression in (107) to (103), the $\frac{e^2}{k}$ cancels, giving

$$-6XZlr^{-3}-2(1-3Z^2)Dr^{-3}-6(3-5Z^2)ZPr^{-4}=-\rho_z D. \quad . \quad . \quad . \quad (108)$$

Solving for l gives a second independent value for this variable, which may be equated to that already obtained from the x-component in (106), and thus l is eliminated. We have

$$l=\frac{\rho_z/2-(1-3Z^2)r^{-3}}{3XZr^{-3}}D-\frac{3-5Z^2}{X}Pr^{-1}. \quad . \quad . \quad (109)$$

XVI. *The Value of* "D."

Upon equating (106) and (109) to eliminate l, we obtain the rather long expression,

$$\frac{9X^2Z^2r^{-6}-[(2-3Z^2)r^{-3}+\frac{1}{4}\rho_x][\frac{1}{2}\rho_z-(1-3Z^2)r^{-3}]}{3XZr^{-3}[(2-3Z^2)r^{-3}+\frac{1}{4}\rho_x]}D$$

$$=\frac{3(1-5Z^2)X^2Pr^{-4}-[(2-3Z^2)r^{-3}+\frac{1}{4}\rho_x](3-5Z^2)Pr^{-1}}{X[(2-3Z^2)r^{-3}+\frac{1}{4}\rho_x]} \quad . \quad . \quad . \quad (110)$$

and by multiplying out the quantities in parentheses and reducing, the value of D obtained from this is

$$D=-3ZPr^{-4}\frac{(3-Z^2)r^{-3}+\frac{1}{4}(3-5Z^2)\rho_x}{2r^{-6}-[\frac{1}{2}(2-3Z^2)\rho_z-\frac{1}{4}(1-3Z^2)\rho_x]r^{-3}-\frac{1}{8}\rho_x\rho_z} \quad . \quad . \quad . \quad (111)$$

The expression for l in (106) involves the constant ρ_x, while that in (109) involves ρ_z; but the resulting expression for D involves both constants. To determine an equilibrium position for the two atoms does not depend so much upon the absolute values of the two constants as upon their relative values, and so far as can now be determined, their ratio may have any value. Let p denote this ratio, such that

$$\rho_z = p\rho_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (112)$$

If an equilibrium is obtained when using certain assumed values of this ratio p, and if it is not obtainable when using quite different values of the ratio, it is legitimate to assume that the ratio that gives the equilibrium shall have the preference, and it is proper to search for such a value of the ratio as will give a definite position of equilibrium. It has been found that a ratio of $p=1/2$ gives a definite solution, but that with a ratio of 1/4 there has been no success in finding an equilibrium position. This is quite different from stating that there is none, however; for the labour involved in a search for the equilibrium position after adopting some definite value for the ratio p is very great, so that the number of these ratios that has been tried is necessarily quite limited. We may content ourselves that a ratio has been found that produces any equilibrium at all. The reasons for this will appear when the process followed is given in more detail.

Therefore, adopting for the present the ratio $p=1/2$, the value of D in (111) reduces to

$$D = -3ZPr^{-4}\frac{(3-Z^2)r^{-3}+\frac{1}{4}(3-5Z^2)\rho_x}{2r^{-6}-\frac{1}{4}\rho_x r^{-3}-\frac{1}{16}\rho_x^2}. \quad . \quad . \quad (113)$$

From this it is evident that D must pass through all values from $-\infty$ to $+\infty$ according to the relative positions of the two atoms. D is evidently zero when the numerator of (111) is zero. This is independent of the ratio p, whence for any value of this ratio we have $D=0$ when

$$r^{-3} = -\frac{1}{4}\rho_x\frac{3-5Z^2}{3-Z^2}. \quad . \quad . \quad . \quad . \quad . \quad (114)$$

This equation is plotted in polar coordinates in terms of Z and r in fig. 7, the curve marked "$D=0$." When $Z=1$ and the two atoms are in the coaxial position, then

$$r^{-3} = \frac{1}{4}\rho_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115)$$

And again, when the denominator of (113) is zero, then $D=\infty$, and we have

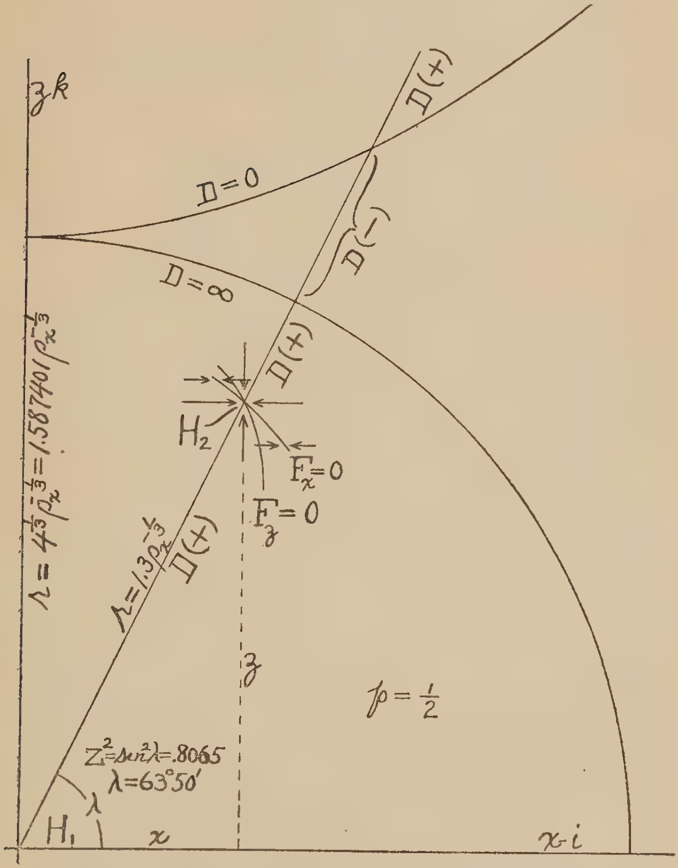
$$2r^{-6}-\frac{1}{4}\rho_x r^{-3} = \frac{1}{16}\rho_x^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (116)$$

which is independent of the direction cosine, Z; and hence

D has the same infinite value at one fixed radius, r, for all angles or positions of the two atoms, r being the root of this equation. Solving, we find the two roots to be

$$r^{-3}=\tfrac{1}{4}\rho_x \quad \text{or} \quad -\tfrac{1}{8}\rho_x. \quad . \quad . \quad . \quad . \quad (117)$$

Fig. 7.



Illustrating the position of stable equilibrium for the two atoms of one hydrogen molecule.

The negative root has no physical significance, and the positive root is the same value as that above obtained in (115). The circle which this represents is shown in fig. 7 and marked "D=∞." The curves for D=0 and for D=∞ meet on the axis where Z=1. This is a critical point where both the numerator and the denominator of D in (113) have become zero. The value of D when $Z=1$ may be evaluated by putting $Z=1$ in that equation, giving

$$D=-3Pr^{-4}\frac{2r^{-3}-\frac{1}{2}\rho_x}{2r^{-6}-\frac{1}{4}\rho_x r^{-3}-\frac{1}{16}\rho_x{}^2}. \quad . \quad . \quad . \quad (118)$$

Now when $r^{-3}=\frac{\rho_x}{4}$ both the numerator and the denominator are zero, but the numerator is an exact factor of the denominator; and when this vanishing factor is cancelled, we have

$$D=-3Pr^{-4}\frac{1}{r^{-3}+\frac{1}{8}\rho_x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (119)$$

whence

$$D=\frac{2}{(4)^{1/3}}(-P\rho_x^{1/3})=1{\cdot}26(-P\rho_x^{1/3}) \quad . \quad . \quad (120)$$

It may be well to emphasize at this point that the meaning of the values of l and of D which are contemplated here is that, if the two atoms are placed in any given positions, the values of l and D must be those given by (109) and (113) for these positions, provided there exists any equilibrium for the two atoms at this point. An infinite value for l or D is manifestly impossible, so the interpretation is that there can be no equilibrium anywhere on the circle of radius

$$r=(4)^{1/3}\rho_x^{-1/3}=1{\cdot}587401\,\rho_x^{-1/3}, \quad . \quad . \quad . \quad (121)$$

because l and D never can be great enough to satisfy the conditions. The equilibrium position must lie elsewhere.

The value of D along any radius vector from the origin is negative between the circle where $D=\infty$ and the curve where $D=0$. It changes sign at these curves and becomes positive at distances greater than where $D=0$, and less than where $D=\infty$. The equilibrium position of the two atoms is evidently directly dependent upon the absolute values of the atomic constants, ρ_x and ρ_z, and the universal distance of 10^{-8} cm. between the two nearest atoms of a molecule is thus shown to depend in a very direct manner upon these atomic constants, and this in itself is sufficient reason for the existence of a universal distance. In finding the equilibrium position it is more convenient to reject or omit the constant multiplier throughout the work and then restore it again at the conclusion in the manner now to be described.

It has been shown that at one critical point r^{-3} depends directly upon ρ_x with a small multiplier, and that r depends upon $\rho_x^{-1/3}$. So we may say in general that

$$r=u\rho_x^{-1/3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (122)$$

where u may now be considered to represent the distance between the two atoms on a different scale if we choose.

And, similarly, we have shown that l and D each depend upon the quantity $(-\mathrm{P}\rho_x^{1/3})$ with a small multiplier, this being a positive quantity since P is negative. Hence we may write

$$l = l'(-\mathrm{P}\rho_x^{1/3}) \quad \text{and} \quad \mathrm{D} = \mathrm{D}'(-\mathrm{P}\rho_x^{1/3}), \quad . \quad . \quad (123)$$

and consider l' and D' as the small displacements in terms of a different unit. With these substitutions for r, l, and D in (106) we obtain

$$l' = \frac{3\mathrm{XZ}u^{-3}\mathrm{D}' + 3(1-5\mathrm{Z}^2)\mathrm{X}u^{-4}}{(2-3\mathrm{Z}^2)u^{-3} + \frac{1}{4}}, \quad . \quad . \quad . \quad (124)$$

where the constant ρ_x does not appear. And, similarly (109) becomes

$$l' = \frac{\frac{1}{4} - (1-3\mathrm{Z}^2)u^{-3}}{3\mathrm{XZ}u^{-3}}\mathrm{D}' + \frac{3-5\mathrm{Z}^2}{\mathrm{X}}u^{-1}, \quad . \quad . \quad (125)$$

and (113) becomes

$$\mathrm{D}' = 3\mathrm{Z}u^{-4}\frac{(3-\mathrm{Z}^2)u^{-3} + \frac{1}{4}(3-5\mathrm{Z}^2)}{2u^{-6} - \frac{1}{4}u^{-3} + \frac{1}{16}}. \quad . \quad . \quad (126)$$

XVI. *The Simplified Equations of the Force of the Second Atom upon the First.*

The final test of the equilibrium positions of the two atoms of the molecule must be that the complete equations for F_x and F_z, (99) and (100), are fully satisfied in addition to the two equations (125) and (126), these thus forming a set of four simultaneous equations containing but four variables, l', D', Z, and u.

When numerical values are introduced, many of the terms of (99) and (100) are seen to be quite negligible, and, in fact, they reduce to the following after substituting for l, D, and r their equivalents in (122) and (123):—

$$\underset{\mathrm{H}_2 \text{ on } \mathrm{H}_1}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\{[-3(2-5\mathrm{Z}^2)\mathrm{X}l'^2 + 6(4-5\mathrm{Z}^2)\mathrm{Z}l'\mathrm{D}'$$
$$+3(1-5\mathrm{Z}^2)\mathrm{X}\mathrm{D}'^2]u^{-4}$$
$$+[6(4-35\mathrm{Z}^2+35\mathrm{Z}^4)l' - 30(3-7\mathrm{Z}^2)\mathrm{XZD}']u^{-5}$$
$$-45(1-14\mathrm{Z}^2+21\mathrm{Z}^4)\mathrm{X}u^{-6}\ldots\}\mathrm{P}^2\rho_x^2; \quad . \quad (127)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\{[-3(4-5\mathrm{Z}^2)\mathrm{Z}l'^2 - 6(1-5\mathrm{Z}^2)\mathrm{X}l'\mathrm{D}'$$
$$+3(3-5\mathrm{Z}^2)\mathrm{ZD}'^2]u^{-4}$$
$$+[30(3-7\mathrm{Z}^2)\mathrm{XZ}l' + 6(3-30\mathrm{Z}^2+35\mathrm{Z}^4)\mathrm{D}']u^{-5}$$
$$-15(15-70\mathrm{Z}^2+63\mathrm{Z}^4)\mathrm{Z}u^{-6}\ldots\}\mathrm{P}^2\rho_x^2. \quad . \quad (128)$$

The whole of the r^{-4} terms has been retained, but the r^{-5} and r^{-6} terms have been much simplified without sacrificing any accuracy by omitting the l^3 and the l^2 D parts in the r^{-5} terms, since these are negligible as compared with Pl or PD, and in the r^{-6} terms all parts are omitted as negligible except the P^2 terms. The latter are the same electrostatic terms as given above in (70) and (71) for symmetrical atoms where l and D were supposed to be zero. If l' and D′ are each put equal to zero in (99) and (100), the whole force reduces to these important r^{-6} terms as formerly.

XVII. *The Process of Computation of the Equilibrium Position.*

The process of computation of the equilibrium position of the two atoms in the molecule may be outlined as follows. The immediate object is to find the locus of all points where the x-component of the force in (127) vanishes, plotting this as a curve. The locus of all points where the z-component vanishes is then plotted as a second curve. The total electrostatic force upon the first atom due to the second, or on the second due to the first, is then zero at all the points of intersection of these two curves, which give the equilibrium positions. Some of these intersections may correspond to unstable, and others to stable, positions; and since we are only interested in the stable positions each point must be examined to prove whether there is stability or not.

Since it requires a considerable amount of computation to obtain even a single point on either the $\mathrm{F}_x=0$ or the $\mathrm{F}_z=0$ curves, it is evident that the work is magnified many fold to trace these curves throughout the whole quadrant. This is our apology for not giving the curves complete throughout the quadrant, even for one single value of p, the ratio of the two constants ρ_z and ρ_x. Let us first assume a definite radius vector corresponding to some fixed value of Z, say such that $\mathrm{Z}^2=0{\cdot}8$. Then (124) and (125) reduce to

$$l'=\frac{1{\cdot}2u^{-3}\mathrm{D}'-4{\cdot}02489u^{-4}}{-0{\cdot}4u^{-3}+0{\cdot}25}, \quad . \quad . \quad . \quad . \quad (129)$$

$$l'=\frac{0{\cdot}25+1{\cdot}4u^{-3}}{1{\cdot}2u^{-3}}\mathrm{D}'=\frac{u^{-1}}{0{\cdot}44721}. \quad . \quad . \quad (130)$$

The expressions for the forces in (127) and (128) become

$$\underset{\substack{H_2 \text{ on } H_1\\ Z^2=0\cdot8}}{F_x} = \frac{e_2}{k}\{[2\cdot6833l'^2-4\cdot02489D'^2]u^{-4} + [-9\cdot6l'+31\cdot2D']u^{-5}-65\cdot2032u^{-6}\}P^2\rho_x{}^2, \quad . \quad . \quad . \quad . \quad (131)$$

$$F_z = \frac{e^2}{k}\{[8\cdot04978l'D'-2\cdot6833D'^2]u^{-4} + [-31\cdot2l'+8\cdot4D']u^{-5}+9\cdot1232u^{-6}\}P^2\rho_x{}^2. \quad . \quad . \quad . \quad . \quad (132)$$

Some arbitrary value of u may now be selected, say $u=1\cdot3$, and l' and D' computed by (129) and (130). The resulting numerical values are

$$l' = 3\cdot09 \quad \text{and} \quad D' = 2\cdot961. \quad . \quad . \quad . \quad (133)$$

Using these numerical values, (131) and (132) become term by term

$$\underset{\substack{H_2 \text{ on } H_1\\ Z^2=0\cdot8\\ u=1\cdot3}}{F_x} = \frac{e^2}{k}\left\{\overset{r^{-4}\text{ term}}{-3\cdot392}+\overset{r^{-5}\text{ term}}{16\cdot81}-\overset{r^{-6}\text{ term}}{13\cdot52}\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(0\cdot102)P^2\rho_x{}^2, \quad . \quad . \quad . \quad (134)$$

$$F_z = \frac{e^2}{k}\left\{17\cdot55 \; -19\cdot27+1\cdot982\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(0\cdot262)P^2\rho_x{}^2. \quad . \quad . \quad . \quad (135)$$

According to this result each component of the force is very small as compared with the individual terms that are added, showing that the position selected is very near to the place where the forces vanish. Because the z-component of the force is positive, it indicates that the distance, u, should be reduced to make this component vanish, since this means an upward force on the first atom at the origin and a downward force on the second atom tending to reduce the distance. Trying another value of u less than $1\cdot3$, say $u=1\cdot29$, gives for l' and D' by (129) and (130),

$$l' = 3\cdot023 \quad \text{and} \quad D' = 2\cdot946, \quad . \quad . \quad . \quad (136)$$

whence by (131) and (132)

$$\underset{\substack{H_2 \text{ on } H_1\\ Z=0\cdot8\\ u=1\cdot29}}{F_x} = \frac{e^2}{k}\left\{\overset{r^{-4}\text{ term}}{-3\cdot758}+\overset{r^{-5}\text{ term}}{17\cdot625}-\overset{r^{-6}\text{ term}}{14\cdot15}\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(-0\cdot283)P^2\rho_x{}^2, \quad . \quad . \quad . \quad (137)$$

$$F_z = \frac{e^2}{k}\left\{17\cdot47-19\cdot52 \; +1\cdot982\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(-0\cdot068)P^2\rho_x{}^2. \quad . \quad . \quad . \quad (138)$$

According to this result, both components of the force have changed sign somewhere between the values of $u=1·3$ and $u=1·29$, so that by interpolation we find approximately that

$$\text{and}\quad \left.\begin{array}{l} F_x = 0 \quad \text{when} \quad u = 1·2972 \\ F_z = 0 \quad \text{when} \quad u = 1·2920 \end{array}\right\} . \quad . \quad . \quad (139)$$

Thus far, but a single point on each $F_x=0$ and $F_z=0$ curve has been found, and the value of Z in the general equations (124) to (128) may next be changed.

Taking $Z^2=0·82$ instead of 0·8 gives

$$l' = \frac{1·15256u^{-3}D' - 3·9457u^{-4}}{-0·46u^{-3}+0·25}, \quad . \quad . \quad . \quad . \quad (140)$$

$$l' = \frac{0·25 + 1·46u^{-3}}{1·15256u^{-3}} D' - 2·593u^{-1}, \quad . \quad . \quad . \quad (141)$$

$$\underset{\substack{H_2 \text{ on } H_1 \\ Z^2=·82}}{F_x} = \frac{e^2}{k}\{[2·6728l'^2 - 0·54332l'D' - 3·9456D'^2]u^{-1}$$
$$+[-6·996l' + 31·58D']u^{-5} - 69·5014u^{-6}\}P^2\rho_x^2, \quad . \quad . \quad . \quad (142)$$

$$F_z = \frac{e^2}{k}\{[0·27166l'^2 + 7·8912l'D' - 2·9883D'^2]u^{-4}$$
$$+[-31·58l' + 11·604D']u^{-5} + 0·527u^{-6}\}P^2\rho_x^2. \quad . \quad . \quad . \quad (143)$$

When $u=1·3$, we find from (140) and (141),

$$l' = 3·023 \quad \text{and} \quad D' = 2·878, \quad . \quad . \quad . \quad (144)$$

and from (142) and (143),

$$\underset{\substack{Z^2=0·82 \\ u=1·3}}{F_x} = \frac{e^2}{k}\Big\{\overset{r^{\ 4}\text{term}}{-4·56} + \overset{r^{-5}\text{term}}{18·82} - \overset{r^{-6}\text{term}}{14·41}\Big\}P^2\rho_x^2 = \frac{e^2}{k}(-0·15)P^2\rho_x^2, \quad . \quad . \quad (145)$$

$$F_z = \frac{e^2}{k}\Big\{+16·23 - 16·74 + 0·1093\Big\}P^2\rho_x^2 = \frac{e^2}{k}(-0·40)P^2\rho_x^2. \quad . \quad . \quad . \quad (146)$$

In order to show how the various terms vary it has seemed best to give these computations in some detail, and so, when u is increased from 1·3 to 1·31, we find instead of (144)

$$l' = 3·077 \quad \text{and} \quad D' = 2·883, \quad . \quad . \quad . \quad (147)$$

and instead of (145) and (146), we find

$$\underset{\substack{Z^2=0\cdot82\\ u=1\cdot31}}{F_x}=\frac{e^2}{\mathrm{k}}\{-4\cdot18+18\cdot03-13\cdot77\}P^2\rho_x{}^2=\frac{e^2}{\mathrm{k}}(+0\cdot80)P^2\rho_x{}^2, \quad . \quad . \quad . \quad (148)$$

$$F_z=\frac{e^2}{\mathrm{k}}\{+16\cdot21-16\cdot51-0\cdot1045\}P^2\rho_x{}^2=\frac{e^2}{\mathrm{k}}(-0\cdot20)P^2\rho_x{}^2. \quad . \quad . \quad . \quad (149)$$

The x-component changes sign from $-$ to $+$ between these two values of u, and by interpolation we find that

$$\text{When } Z^2=0\cdot82, \quad F_x=0 \text{ at } u=1\cdot3065. \quad . \quad . \quad (150)$$

The z-component is still negative, but smaller than when $u=1\cdot3$, and upon trying $u=1\cdot32$, we find

$$l'=3\cdot174 \quad \text{and} \quad D'=2\cdot910, \quad . \quad . \quad . \quad (151)$$

and that $F_z=\frac{e^2}{\mathrm{k}}(0\cdot085)P^2\rho_x{}^2$, having changed sign between 1·31 and 1·32. By interpolation we have

$$\text{When } Z^2=0\cdot82, \quad F_z=0 \text{ at } u=1\cdot317. \quad . \quad . \quad (152)$$

These results show that when $Z^2=0\cdot82$, the $F_z=0$ curve lies outside of the $F_x=0$ curve, whereas, when $Z^2=0\cdot8$, as first assumed above, the $F_x=0$ curve lies outside of the $F_z=0$ curve. Consequently the two curves intersect at some point between $Z^2=0\cdot8$ and $Z^2=0\cdot82$. By interpolation the probable intersection occurs at approximately

$$\left.\begin{array}{lll} Z^2=0\cdot8065 & \text{and} & u=1\cdot30, \\ l'=3\cdot066 & \text{and} & D'=2\cdot935. \end{array}\right\} \quad . \quad . \quad (153)$$

These $F_x=0$ and $F_z=0$ curves are shown in fig. 7 computed between the values $Z^2=0\cdot7$ and $Z^2=0\cdot86$, showing the intersection at the point given by (153) approximately. This point represents one of stable equilibrium rather than unstable, and it may be regarded as one solution of the problem. The stability may be shown by examining the directions of the forces on either side of the curves of zero force. When the radius vector is greater than the value corresponding to the $F_x=0$ curve, the x-component of the force of H_2 on H_1 is positive and of H_1 on H_2 negative, as indicated by the horizontal arrows directed towards the curve in the figure. Also for radii smaller than those corresponding to the curve the force changes sign and the arrows are again directed towards the curve. Any displacement to the right or left of this curve sets up forces that tend to bring the atom back to the curve, showing stability for the x-component.

And similarly for the z-component of the force. All forces surrounding the point of equilibrium are thus directed towards this point thus showing stability. The atoms tend to return to this position for displacements in any direction.

XVIII. *Absolute Values.*

While no way has been found to obtain a numerical value for the constant ρ_x in an *a priori* manner, this is not true of the other constant ρ_z. The definition of this constant is contained in the assumption made in (107), which is repeated here, that the force upon C is proportional to D; namely,

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_z} = -\frac{e^2}{\mathrm{k}}\rho_z \mathrm{D}, \quad . \quad . \quad . \quad . \quad . \quad (107)$$

so the constant may be said to denote this force when D is unity.

But in (25) it was shown that the work done by the electron A in forming the molecule is

$$-\frac{e^2}{\mathrm{k}}(30{\cdot}7\times 10^{24})(b_2-b) = -6{\cdot}964\times 10^{6}(b_2-b), \quad . \quad (154)$$

while the work done upon B during the same interval is

$$-\frac{e^2}{\mathrm{k}}(30{\cdot}7\times 10^{24})(b_1-b). \quad . \quad . \quad . \quad . \quad (155)$$

The sum of these energies, the first being negative and the second positive, was given in (74) as representing the work done by A over and above that done upon B, which represents one-half of the total energy of dissociation of the molecule. On the other hand, the difference between these energies is

$$-\frac{e^2}{\mathrm{k}}(30{\cdot}7\times 10^{24})\mathrm{D}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (156)$$

Since each of the above energies is large as compared with their difference, the last expression is very approximately double the energy change for each electron, disregarding the sign. One-half of this, then, represents the energy given up by A and received by B. So the energy change to decrease the semi-minor axis of B by the amount a, or to increase that of A by the same amount (see (75) and (76), is

$$\frac{1}{2}\frac{e^2}{\mathrm{k}}(30{\cdot}7\times10^{24})\,\mathrm{D}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (157)$$

But for a unit distance, or for D equal to unity, the energy and the force required to make this change in the energy are numerically equal to each other. The force is given by one-half of (107) above, since the force on the positive charge is the sum of that on the two electrons; whence it follows that the constant ρ_z is the numeric that occurs in (156), and we have

$$\rho_z = 30{\cdot}7\times10^{24}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (158)$$

At the position of equilibrium found above we have

$$r = u\rho_x^{-1/3} = 1{\cdot}3\rho_x^{-1/3}, \text{ or } r^{-3} = 0{\cdot}455\rho_x \quad . \qquad (159)$$

and

$$\mathrm{D} = \mathrm{D}'(-\mathrm{P}\rho_x^{1/3}) = 2{\cdot}935(-\mathrm{P}\rho_x^{1/3}). \quad . \quad . \quad . \qquad (160)$$

If $\rho_z=\rho_x/2$, as was previously assumed in the special case in which the equilibrium was obtained, then

$$r^{-3} = 0{\cdot}91\rho_z = 0{\cdot}91\times30{\cdot}7\times10^{24} = 27{\cdot}94\times10^{24}$$

and

$$r = 0{\cdot}3295\times10^{-8}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \qquad (161)$$

and

$$\begin{aligned}\mathrm{D} &= 2{\cdot}935\times1{\cdot}25\times10^{-26}\times3{\cdot}945\times10^{8}\\ &= 14{\cdot}47\times10^{-18}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (162)\end{aligned}$$

and

$$\begin{aligned}l &= 3{\cdot}066\times1{\cdot}25\times10^{-26}\times3{\cdot}945\times10^{8}\\ &= 15{\cdot}11\times10^{-18}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (163)\end{aligned}$$

According to this result, the order of magnitude of the distance between the atoms is 10^{-8} cm. in round numbers, which is in accord with the known facts emphasized at the beginning of this paper. The precise value cannot, of course, be obtained until the other constant, ρ_x, is computed in a direct manner from the electrostatic forces; but it is subject to computation, as before stated, on the basis of the atom model.

For example, if an equilibrium were obtained when the ratio p is made equal to unity and $\rho_z=\rho_x$, then the value of r would have been, instead of $\cdot3295\times10^{-8}$ cm., according to (159),

$$r=u(0{\cdot}322)10^{-8}; \quad . \quad . \quad . \quad . \quad . \quad . \qquad (164)$$

and if the equilibrium distance u came out $1{\cdot}5525$ instead of

1·3 as above, which is quite possible, then the distance r comes out

$$r=0·5\times10^{-8}\text{ cm.}, \quad . \quad . \quad . \quad . \quad . \quad (165)$$

which is the value that agrees with the experimental evidence as well as any other. The reason for not working out many cases of the equilibrium is just because we lack any *a priori* knowledge of the unknown constant ρ_x. But it is probable that it does not differ greatly from ρ_z, and by means of this the order of magnitude of the distance is established theoretically as depending directly upon the property of the electron.

Using the same value of the ratio, $p=1/2$, as before, which is as good as another so far as we know, it is interesting to study the order of magnitude of the small displacements l and D. According to (77) and (162), we find

$$D=b_2-b_1=2a+h=14·47\times10^{-18}\text{ cm.}, \quad . \quad (166)$$

and the value of h was found in (80) to be $0·4164\times10^{-18}$ cm. Hence

$$a=7·027\times10^{-18}\text{ cm.}, \quad . \quad . \quad . \quad . \quad . \quad (167)$$

which represents the total change in the semi-minor axis of electron B as the molecule is formed from free atoms. The expansion of the semi-axis of electron A is greater by the amount h, so that the new semi-axes, which were assumed as exactly 10^{-13} cm. in the free atom, become

$$\left.\begin{array}{ll}\text{for A} & b_2=1·000,074,43\times10^{-13}\text{ cm.},\\ \text{and for B} & b_1=0·999,929,73\times10^{-13}\text{ cm.}\end{array}\right\} \quad . \quad . \quad (168)$$

In making these changes the electron A gave up an amount of energy

$$\Delta E_A=-6·964\times10^6(b_2-b)=-51·83\times10^{-12}\text{ erg}, \quad . \quad (169)$$

while the electron B absorbed an amount of energy

$$\Delta E_B=-6·964\times10^6(b_1-b)=+48·93\times10^{-12}\text{ erg}. \quad . \quad (170)$$

The sum of this negative and positive energy represents the part of the original energy content of the two electrons that is used in forming the molecule, which is

$$\begin{aligned}\Delta E_A+\Delta E_B&=-6·964\times10^6[(b_2+b_1)-2b]\\ &=-6·964\times10^6h=-2·9\times10^{-12}\text{ erg}. \quad . \quad . \quad (171)\end{aligned}$$

This is just half of the energy of dissociation of the molecule, namely $5·8\times10^{-12}$ erg as determined experimentally, and the same value is obtained by adding (169) and (170).

According to this, nearly seventeen times as much energy is passed across from the electron A to B as is used in forming the molecule—that is, in binding the second atom to the system. The actual change in the minor axis of either electron is minutely small as compared with the minor axis itself, the minor axis being about 14,200 times greater. It has been shown conclusively, however, that on the basis of the electrostatic forces alone this very small asymmetry of the two electrons is responsible for the formation of the molecule.

The displacement of the positive charge C off from the centre line of the two electrons represented by $l/2$ is given by (163) above. Bearing in mind that the semi-major axis of the positive charge (6) is $7{\cdot}054 \times 10^{-16}$ cm., it appears that this displacement is only a small fraction of its own radius, about the ninety-third part of it. This fact is sufficient to show that it would be futile to attempt to derive the constant ρ_x by assuming that the positive charge may be regarded as a point charge, for only the minutest portion of the charge crosses the centre line joining the two electrons. The major portion of it still remains on either side after the displacement, and yet this very small displacement, together with the displacement D discussed above, is sufficient to account for the formation of the molecule.

XIX. *The Stress within the Atom.*

The force upon the positive charge C in the direction of the x-axis or equatorial direction is given by (104), which now becomes numerically

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}} \rho_x \frac{l}{2} = \frac{e^2}{\mathrm{k}} 464 \times 10^6. \quad . \quad . \quad . \quad (172)$$

This is a comparatively large force, being the equivalent of the repulsion between two electrons at a distance of only about $4{\cdot}6 \times 10^{-5}$ cm. from each other. On the other hand, for comparison the order of magnitude of the forces upon the whole atom near to their position of equilibrium by (127) and (128) is

$$\frac{e^2}{\mathrm{k}} \mathrm{P}^2 \rho_x^{\,2} = \frac{e^2}{\mathrm{k}} (590 \times 10^{-3}), \quad . \quad . \quad . \quad (173)$$

which is nearly 10^9 times smaller than the forces producing the internal strain.

XX. *The Coaxial Position.*

It may be shown that there can be no equilibrium for the two atoms of the molecule when in the coaxial position, no matter what the relative values of the constants ρ_x and ρ_z may be. These constants are essentially positive, and their ratio, p, is also necessarily positive. Putting $Z=1$ and $X=0$ in (102) and equating to (104) gives

$$2lr^{-3}=\rho_x\frac{l}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (174)$$

from which l cancels, giving the same result as in (115) above, and which must hold true for any and every value of l. That is to say, l cannot be determined from (102). And again making $Z=1$ and $X=0$ in (127) and equating to zero gives

$$-6l'D'u^{-4}+24l'u^{-5}=0, \quad . \quad . \quad . \quad . \quad (175)$$

whence

$$D'=4u^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (176)$$

But when (103) is equated to (107) and $Z=1$, $X=0$, we have

$$4Dr^{-3}+12Pr^{-4}=-\rho_z D=-p\rho_x D. \quad . \quad . \quad (177)$$

Since r^{-3} must be $\frac{1}{4}\rho_x$ at the equilibrium position according to (174), it follows that

$$D'=\frac{3}{(4)^{1/3}}\,\frac{1}{1+p}=\frac{D}{(-P\rho_x^{1/3})}. \quad . \quad . \quad . \quad (178)$$

When $p=1/2$, as was assumed in the case previously discussed, then

$$D=\frac{2}{(4)^{1/3}}(-P\rho_x^{1/3}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (179)$$

which is the same value as in (120) for this particular case. But the two values found for D′ in (176) and (178) must agree, so that

$$D'=4u^{-1}=4\frac{r^{-1}}{\rho_x^{1/3}}=\frac{4}{(4)^{1/3}}=\frac{3}{(4)^{1/3}}\cdot\frac{1}{1+p}, \quad . \quad (180)$$

whence $p=-1/4$, which is impossible, as before stated, because of the negative sign. Hence there exist no values of the constants ρ_x and ρ_z that will produce an equilibrium when the atoms have the coaxial position.

XXI. *Available and Unavailable Energy.*

There has been a renewed discussion recently of the old topic of releasing interatomic energy to be used for practical commercial purposes, some inclining to the view that the energy is so securely locked within the atoms that it will never be possible to release it, and others claiming that they have already attained the proof experimentally that the long-sought goal is within the realm of possibility. It seems worth while to examine this question once more in the light of the points that have been made in this paper. Both opinions seem likely to be substantiated, paradoxical as this may be. The total energy content of any mass of matter is expressed by mc^2, where m is its mass and c the velocity of light. By far the greater part of this is the energy content of the elementary bodies, the positive and negative charges, in their free states. This is not simply interatomic energy, but it is interelectronic energy as well.

In this paper it has been pointed out that in forming atoms and molecules out of these free elementary bodies some of their original energy content has been used, but that it is an extremely minute portion of the whole. Until we are prepared to admit, therefore, that a much larger part or even the whole energy content of the electrons may be abstracted, then it must remain true that this energy is so securely locked within the atoms that we may never expect to make it available energy for practical purposes. In this sense the first opinion above given is likely to be true.

On the other hand, even that minute portion of the energy content of the electrons, the portion actually given up in forming atoms, may be so much greater than the still smaller energies now available—let us say the energies of combustion, coal energy or chemical energy which is obtainable from an exchange of atoms in molecular structures—even that minute portion may be so much greater than the chemical energy now available that there is much assurance of the possibility of increasing the energy available at present many times. In this sense the second opinion above mentioned is likely to be substantiated, and both opinions may be correct, it depending entirely upon the value of interatomic energy that each had in mind in making the statements.

For example, we may think of 10^{-12} erg as the order of magnitude of the energies available at present derived from altering molecular structures in combustion, etc.—that is, the energy per molecule. This may be compared with the energy of single ionization of the hydrogen atom, about 35×10^{-12} erg, or with the energy of double ionization, which is not known exactly, but is many times greater than the single ionization energy. It seems quite probable that the energy required to separate the elementary fundamental bodies or charges within an atom itself, or to change them about just as is now done with the atoms in molecules, may sometime be used for practical purposes. At any rate, it may be looked upon as available energy in contradistinction to that locked within the electrons which is not available. This available energy may easily be more than 100×10^{-12} erg per atom, or more than 100 times the energy at present made use of, but it probably will never approach 100,000 times as much, at least until an electron may be made to give up all of its energy.

XXII. *Conclusion.*

The question foremost in the minds of all in examining a presentation of any new subject is: What has been accomplished of any practical value? This often reveals an impatience that there are not more practical results immediately in sight or to follow without much delay. If this investigation reveals anything, it is that it requires a considerable amount of patience and perseverance against odds to accomplish anything of value in this most intricate and involved subject. The form of atomic model considered in this paper has been so fruitful in enabling us to arrive at an understanding of so many phenomena that it must commend itself very forcefully to investigators. To have shown that electrostatic forces are quite sufficient to produce the formation of molecules, after the directions of the axes of rotation are taken care of by the electromagnetic forces due to the rotation of the elementary bodies, and that the order of magnitude of the distance between centres of nearest atoms must be of the order of 10^{-8} cm., as it is known to be in fact, is considered to be an important result that may hereafter have practical consequences.

It must be true, however, that we do not know much about even the simplest atoms until it is possible to answer such questions as the following for example:—Why is it that 44,000 small calories of energy are given up as heat per gram-molecule when hydrogen gas and chlorine unite to form HCl? But when nitrogen and oxygen are united together to form nitric oxide (NO) there occurs an absorption of 43,150 small calories of energy per gram-molecule instead of an evolution of energy as heat? Until we have a clear understanding of these phenomena in terms of some atomic model, it cannot be said that we know much about the atoms of nitrogen, oxygen, and chlorine. And so on through a whole list of elements these energy relations are of the greatest importance; but we are not aware of any other form of atomic model that throws any definite light on these questions. By means of the models discussed in this and previous papers, however, there is encouragement to think that some of these questions may receive a very definite answer.

This paper has dealt almost exclusively with the atom of hydrogen, because it is so very much simpler than all others; but it may readily be seen that the same principles apply to other atoms with equal force, although the computations become more complex. Nor has the investigation of hydrogen been completed; we still require the atomic constant ρ_x, which may be computed sometime. Then, too, more of the equilibrium curves similar to those of fig. 7 should be computed, for it is suspected that for some values of the constants there may be more than a single point that shows stability for the two atoms of the molecule. One may even suspect that there are two different equilibrium positions for the atoms in the hydrogen molecule from the behaviour of hydrogen itself. Hydrogen sometimes forms a molecule with three instead of two atoms according to Sir J. J. Thomson's discovery, and this is comparatively unstable. The difference between what is called "nascent hydrogen" and hydrogen may also be connected with these two possible stabilities suspected. The nascent form of hydrogen may be the more unstable form of molecule. This is now, of course, a matter of pure speculation, but it is just such unknown phenomena that supply the incentive to investigation.

Since the equilibrium as between the two atoms of a molecule is dependent upon a balance between the r^{-4}, r^{-5}, and r^{-6} terms of the force series, it should result from experiments in the compression and expansion of solids that the apparent law of force between atoms obeys some power intermediate between -4 and -6, probably the inverse fifth power approximately. This result is in close agreement with the experimental evidence as far as it is known.

And finally it is considered an important result to have shown that there exist constants characteristic of each atom, which are responsible for the universal distance of the order of 10^{-8} cm. between nearest atoms, as well as to have arrived at some understanding of their physical meaning, which reveals the necessity for their existence.

APPENDIX A.—*The Value of* $P = b^2 - \frac{1}{2}\rho a^2$.

For the purpose of approximation to the oblate spheroid by the substitution of the circle-and-point-electron in its stead, it is assumed that the ring is best represented by a circle whose radius is equal to the radius of gyration of the ring. By the ring is meant the part of the spheroid that remains after cutting out an inscribed sphere. The first requirement is then to find the radius of gyration of the ring.

The moment of inertia of the oblate spheroid about its minor axis is, assuming a uniform density throughout its volume,

$$I_{\text{O.S.}} = (\tfrac{4}{3}\pi a_0^2 bd)(\cdot 4 a_0^2), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the first factor being the mass, and the second the square of the radius of gyration of the spheroid.

The moment of inertia of the inscribed sphere is

$$I_S = (\tfrac{4}{3}\pi b^3 d)(\cdot 4 b^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The moment of inertia of the ring excluding the inscribed sphere is the difference between (1) and (2), namely

$$I_R = I_{O.S} - I_S = \tfrac{4}{3}\pi bd(a_0^2 - b^2)a^2 = \tfrac{4}{3}\pi bd(a_0^4 - b^4)(\cdot 4), \quad (3)$$

where a is the radius of gyration of the ring. Hence

$$a^2 = \cdot 4(a_0^2 + b^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where a is also the radius to be found, and which is used in the circle-and-point-electron.

According to (24) the eccentricity of the electron in the atom is $\epsilon = 0{\cdot}9547$, or

$$1 - \epsilon^2 = 1 - 0{\cdot}91145 = 0{\cdot}08855\,; \quad . \quad . \quad . \quad (5)$$

whence by (12)

$$a_0^2 = \frac{b^2}{1-\epsilon^2} = \frac{10^{-26}}{\cdot 08855} = 11{\cdot}3 \times 10^{-26} \quad . \quad . \quad . \quad (6)$$

$$\text{and} \qquad a^2 = \cdot 4(11{\cdot}3 + 1)10^{-26} = 4{\cdot}92 \times 10^{-26}, \quad . \quad . \quad (7)$$

$$\text{or} \qquad a = 2{\cdot}218 \times 10^{-13} \quad \text{and} \quad a_0 = 3{\cdot}36 \times 10^{-13}\ \text{cm.} \quad . \quad (8)$$

Since by (45) above $\rho = \epsilon^2$, we find that

$$\rho a^2 = 0{\cdot}91145 \times 4{\cdot}92 \times 10^{-26} = 4{\cdot}484 \times 10^{-26}. \quad . \quad (9)$$

And hence

$$P = b^2 - \tfrac{1}{2}\rho a^2 = (1 - 2{\cdot}242)10^{-26} = -1{\cdot}242 \times 10^{-26}, \quad (10)$$

which was to be found. The value used in the paper is the even figure $-1{\cdot}25 \times 10^{-26}$.

LXXXIX. *An attempted Electrolytic Separation of the Isotopes of Chlorine and Magnesium.* By JOHN E. G. PILLEY*.

1. AT the Royal Society discussion on Isotopes (Proc. Roy. Soc. 1921) it was suggested by Professor Lindemann that it might be possible to separate isotopic ions by an electrolytic method depending on an expected difference between their migration velocities in solution. If such a difference existed, and if the fastest-moving ions could be isolated, it would be possible to obtain complete separation by this means.

The method depends upon the assumption that the ions are not large compared with the solvent molecules. For unless this were so, their velocity would be uniform and independent of the mass of the ion.

If the ions are of the same order of magnitude as the solvent molecules, the medium in which they move can scarcely be regarded as homogeneous. Although the resultant force of the surrounding molecules will vary between considerable limits, one might reasonably expect that one would obtain a first approximation of their behaviour by treating them as having a free path between collisions with solvent molecules. Hence the migration velocity of the ion, when measured over distances large compared with the molecular distances, could be treated as though it were made up of a large number of free paths over which there was a component of acceleration due to the electric force. Presumably the actual lengths of the free paths of isotopes are identical; and as their masses and velocities and therefore the times spent on such free paths are different, the migration velocities measured over large distances should also be different.

On this basis it is possible to obtain an estimate of the difference of mobility that could be expected.

Let m be the mass of the solvent molecules.

Let M be the mass of the ions.

Let V_m be the observed migration velocity.

Let V_0 be the average velocity due to the field after collision.

Let V_f be the average velocity due to the field before collision.

Let F be potential gradient.

Let E be the charge on the ion.

Let t be the time spent on a free path.

If, as assumed above, the greater part of the ion's change of momentum takes place in the neighbourhood of the solvent molecule, the problem reduces itself to that of an ion moving along a number of free paths terminated by collisions. If we adopt the view that the probability of an ion assuming any direction of motion after collision is equally great, but that the momentum along the axis of motion remains unaltered through collision, we obtain an expression relating the velocities before and after collision. If, as a first approximation, we treat the colliding particles as smooth spheres, then

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* Communicated by the Author.

$$\frac{V_0}{V_f}=\frac{M+\frac{(1-\epsilon)}{2}m}{M+m}, \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where ϵ is the coefficient of restitution.

If t is the time interval between successive collisions, the electric field applied to the ion will produce a change of velocity such that

$$V_f=V_0+\frac{FEt}{M}. \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

Combining these two equations, we find that

$$V_0=FEt\left(\frac{M+m\left(\frac{1-\epsilon}{2}\right)}{Mm\left(\frac{1+\epsilon}{2}\right)}\right). \quad . \quad . \quad . \quad \text{(iii.)}$$

As the acceleration due to the field is uniform, the mean velocity of motion of the ion would be

$$V_a=V_0+\frac{FEt}{2M}. \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

Hence, substituting the value of V_0 from (iii.),

$$V_a=FEt\left(\frac{M+m\left(\frac{1-\epsilon}{2}\right)}{\left(\frac{1+\epsilon}{2}\right)Mm}+\frac{1}{2M}\right)=FEt\left(\frac{2M+\left(\frac{3-\epsilon}{2}\right)m}{(1+\epsilon)Mm}\right). \quad . \quad . \quad . \quad \text{(v.)}$$

If r is the mean relative velocity of ion and solvent molecule, then the time occupied on a free path l will be such that

$$t=\frac{l}{r}.$$

The mean relative velocity is related to the mean velocities of the two colliding particles according to the well known formula of the kinetic theory:

$$r=\frac{3v_1^2+v_2^2}{3v_1},$$

where v_1 is the velocity of the faster-moving particle.

Considering the case where the mass of the ion is greater than that of the solvent molecule $(M>m)$, and where consequently the ion has a smaller average velocity than the solvent molecule, then

$$V_1=\sqrt{\frac{3KT}{m}},$$

$$V_2=\sqrt{\frac{3KT}{M}}.$$

Since $$t=\frac{l}{r}=\frac{3lv_1}{3v_1^2+v_2^2}=\frac{3lM\sqrt{m}}{\sqrt{3KT}(3M+m)},$$

the migration velocity in terms of M and m becomes

$$V_a=FE\left(\frac{2M+\frac{3-\epsilon}{2}m}{(1+\epsilon)Mm}\times\frac{3lM\sqrt{m}}{\sqrt{3KT}(3M+m)}\right)$$

$$=\frac{3FEl}{(1-\epsilon)\sqrt{KTm}}\left(\frac{2M+\frac{3-\epsilon}{2}m}{3M+m}\right).$$

The percentage difference in mobility for unit difference of atomic weight M is therefore

$$\frac{1}{V_a}\frac{dV_a}{dM}=\frac{3}{3M+m}-\frac{2}{2M+\left(\frac{3-\epsilon}{2}\right)m}.$$

The result is slightly different in the case $(M<m)$; that is to say, when the solvent molecule has the smaller velocity. In this case

$$V_a=FE\left[\frac{2M+\left(\frac{3-\epsilon}{2}\right)m}{(1+\epsilon)Mm}\times\frac{3lm\sqrt{M}}{\sqrt{3KT}(Mt+3m)}\right]$$

$$=\frac{3FEl}{(1+\epsilon)\sqrt{3KT}}\times\frac{2M+\left(\frac{3-\epsilon}{2}\right)m}{\sqrt{M}(M+3m)},$$

and consequently

$$\frac{1}{V_a}\frac{dV_a}{dM} = \frac{\frac{3}{2}\sqrt{M}+\frac{3m}{\sqrt{M}}}{\sqrt{M}(M+3m)} - \frac{2}{2M+\left(\frac{3-\epsilon}{2}\right)m}.$$

By substituting actual values of M and m in these equations, an estimate of the separation to be expected can be obtained.

Thus, for instance, in the case of chlorine ions, assuming that there is neither hydration of the ions nor association of the water molecules, namely that $M_1 = 35$, $M_2 = 37$, and $m = 18$, one finds

when $\epsilon = 1$ a difference of ·3 per cent.,
when $\epsilon = 0$ a difference of ·7 per cent.

between the calculated mobilities of the two isotopic ions. If, however, the water is polymerized and consists chiefly of $2(H_2O)$ molecules, a difference of about ·5 per cent. would be expected when $\epsilon = 1$, and 1·0 per cent. when $\epsilon = 0$.

If, lastly, the ions are hydrated and the solvent molecules associated, *e. g.* the ions have masses $(35+36)$ and $(37+36)$ respectively and the solvent molecules are of effective mass 36, one would still expect a difference of ·2 per cent. for $\epsilon = 1$ and ·4 per cent. for $\epsilon = 0$.

Even if the least favourable of these results were valid, a separation should be realizable.

2. *Experimental.*

In order to test whether isotopic mixtures could be resolved on this principle, two series of experiments were carried out: one with chlorine and the other with magnesium.

The method adopted was to allow the ions to move into an electrolyte, initially free from such ions, suspended in a jelly of agar-agar in order to reduce convectional mixing. After a suitable time the jelly was removed and the front boundary reached by the ions was cut off. The atomic weight of the element concerned as represented by these ions was then compared with that of the same element as represented by ions from the middle of the column.

The difference of mobility should be of the order of ·4 per cent. for a difference of two units in atomic weight. If a smaller fraction than this of the total number of ions transported is cut off from the head of the column, one would therefore expect to find a marked difference between their atomic weight and that of the rest of the ions. The scale of the experiments depends on the amount of the material desired; but the "cut" must be such that it is electro-chemically equivalent to less than ·2 per cent. or to ·3 per cent. of the whole time-current product.

A number of tubes 100 cm. long and 1·5 cm. diameter were filled, in the first series of experiments, with a half-normal potassium nitrate solution containing 30 grams of agar-agar per litre. The ends of the tubes fitted into the sides of specially constructed rectangular boxes which formed the anode and cathode compartments, and between which a potential difference of up to 300 volts could be maintained. The solution in the anode cell was prevented from becoming acid with half-normal potash, and similarly that in the cathode department was prevented from becoming alkaline with half-normal hydrochloric acid. The levels of the liquids in the two compartments were kept the same by means of a long, narrow gauge siphon. The tubes which lay horizontally between the two boxes were kept cool with a current of cold water, and thus the temperature of the electrolyte was prevented from rising unduly. As, however, both mobility and thermal diffusion are proportional to the square root of the absolute temperature, the effect of change in temperature is not serious.

In the earlier experiments, when the boundary had almost reached the anode end of the tube, electrolysis was stopped and the jelly pushed back so that the Cl/NO_3 boundary was at the cathode end again, and that the chlorine boundary might traverse a further length of nitrate solution.

The electrolysis was carried out for about fourteen hours with a voltage gradient of 3 volt/cm.

At the end of the experiment the position of the chlorine boundary was located by placing the jelly in an acid silver solution and observing the cloud of silver chloride formed.

As the absolute velocity of NO_3 ions is less than that of Cl ions, the front of the advancing Cl band was diffuse; and in order to estimate the amount being cut off, several successive "cuts" were made from each tube and the corresponding cuts from each identified by matching the intensities of the silver chloride clouds formed. The amount each cut contained was estimated subsequently.

A subsidiary series of experiments was carried out with potassium hydroxide instead of potassium nitrate in the tubes, and in these, since the OH ion has a much greater velocity than the Cl ion, a sharp boundary between the OH and Cl ions was produced.

The "front section" chlorine "cuts" from these two experiments were added and the atomic weight determined.

As each cut of the leading section was made, an equivalent amount was taken from half-way down the tube, and this provided material for a check atomic weight.

Chlorine was precipitated from both "front" and "middle" specimens as silver chloride, and this when thoroughly washed and dried was reduced in a stream of pure dry hydrogen prepared by the electrolysis of baryta water. The hydrochloric acid evolved was collected in pure conductivity water; and it was from these solutions that the pure silver chloride for atomic weight determinations was precipitated by the addition of just less than the amount of silver nitrate necessary for complete precipitation of the chlorine. The ratio AgCl : Ag was then determined by reducing this silver chloride after it had been carefully washed and dried.

For this reduction a double furnace was used which contained two tubes of pyrex glass side by side, into which small light silica boats containing the two samples of silver chloride to be compared could be placed. The tubes were enclosed in a nickel case in which they were heated by the same electric heater. The temperature was read with a thermo-junction in a thin glass tube just over the surface of each of the boats containing silver chloride. The precipitation and washing processes were conducted in a safe orange light, and nearly equal weights of the two kinds were placed in silica boats, also of almost the same weight. The chloride was finally dried in the dark in a stream of dry air. When the two specimens became constant in weight, the chloride was reduced in a stream of pure hydrogen and the silver formed carefully weighed.

Weighings were carried out on a sensitive assay balance, with the usual precautions for great accuracy. Not only were the weights of the two boats containing the samples compared, but the absolute weight of each was measured. The amounts used were small enough to render the correction for buoyancy almost negligible.

In four preliminary experiments with silver chloride prepared from pure silver nitrate it was found possible to obtain values of the atomic weight differing by less than ·1 per cent. of the accepted value of 35·46. Chlorine was re precipitated as silver chloride from the hydrochloric acid collected from the reduction, and used for a further determination of atomic weight.

The values obtained for successive atomic weight determinations were :—

Front section.	Middle.
35·49	35·45
35·44	35·48
35·48	35·41

These results seemed definitely to indicate that no separation of the isotopic chlorine ions, of the order expected, had been effected. Since it seemed possible that there might be a specific action between the chlorine and the jelly, it was decided to make a second series of experiments with magnesium ions.

The difference of mobility to be expected is of the same order as with chlorine.

If $Mg=24$,
$H_2O=18$, the difference of mobility should be ·6 per cent. $(\epsilon=1)$.

If $MgH_2O=42$,
$2H_2O=36$, the difference of mobility should be ·4 per cent. $(\epsilon=1)$.

The experiment was made under almost the same conditions as in the case of chlorine. Tubes of the same dimensions were used, and filled with a jelly containing half-normal solution of ammonium sulphate. The anode compartment was filled with magnesium sulphate in which was suspended a large excess of magnesium oxide.

The position of the magnesium boundary in the tube at the end of the experiment was found by treating the jelly with an alkaline solution of ammonium oxalate. The fraction cut off was, as with chlorine, about 2 per cent. of the total amount transported by the current. At the same time, sections containing approximately the same weight of magnesium were cut off from the middle of the column of jelly impregnated with magnesium, to provide material for a check atomic weight.

The specimens of magnesium obtained from these two sources were purified alongside each other by identical chemical processes, and their atomic weights determined simultaneously. The first step in the purification was to calcine the jelly and to dissolve the residue in dilute sulphuric acid. The solution was next filtered and evaporated to drive off any excess of sulphuric acid.

The solution was then treated with ammonia and ammonium sulphide, and allowed to stand several hours in contact with the precipitant.

Calcium was next removed as oxalate from the filtrate by the method described by Blasdale, and the magnesium precipitated as phosphate with ammonia and sodium phosphate.

After thorough washing of the phosphate, the magnesium was obtained, in soluble form, by fusing with purest sodium carbonate. The washed carbonate was next dissolved in sulphuric acid. Traces of sodium remaining were removed by repeated precipitation of the magnesium as carbonate with an alcoholic solution of ammonia and ammonium carbonate and by thorough washing.

The magnesium carbonate was converted to sulphate, and finally purified by fractionation from a mixture of re-distilled alcohol and water.

The ammonia and ammonium sulphide were made by saturation of conductivity water with ammonia and sulphuretted hydrogen gases.

Pyrex vessels were used in the earlier part of the purification and platinum in the final processes.

The atomic weight of the magnesium in the two samples of magnesium sulphate purified in the above manner was then determined by converting to oxide according to a method used by Mr. A. C. Egerton in this laboratory. The accuracy of the determinations by many investigators of the ratio $MgSO_4 : MgO$ had been vitiated by occlusion of gas by the oxide obtained by ignition of the anhydrous sulphate. In order to overcome this difficulty, both the sulphate and the oxide were weighed in a high vacuum. For this purpose special light weighing bottles of Pyrex glass were constructed. The lids of the bottles carried small taps through which the bottles could be exhausted while the small platinum crucibles containing the sulphate or oxide were still hot. Both the lids and the taps were greased with special tap grease, and the bottles held a hard vacuum without leak. The total weight of the bottles with their crucibles was about twelve grams.

Approximately equal weights of the two samples of magnesium sulphate were weighed into two platinum crucibles, which were heated side by side in an electric resistance furnace to 600° until, after transferring to the weighing bottle, the weight became constant. The dry sulphate was next converted into oxide by heating the crucibles again side by side to 1150–1200° in an alundum muffle for several hours, the temperature being measured with an optical pyrometer and the oxide being weighed as described.

In a preliminary series of six determinations on some specially purified magnesium sulphate, Mr. Egerton has obtained agreement by this method in each case within ·03 units of the accepted value 24·32. The method was therefore deemed sufficiently accurate for the present purpose (where differences of about $\frac{1}{2}$ per cent. were being looked for), although the quantities available for the determinations were somewhat less than those used by Mr. Egerton.

In the first determinations the quantities of material (200 milligrams) were found to be insufficient to give reliable results, and further electrolyses were made; and after adding the first samples, the whole was re-purified and the atomic weights re-determined. The values obtained were :—

Front section.	Back section.
24·36	24·28
24·12	24·10
24·34	24·30

The values obtained for the atomic weight are affected by the conditions under which the magnesium sulphate is heated. The values in the second determination are, for example, both too low. As, however, the two specimens of magnesium compound were always subjected to the same treatment, the correspondence of the two values bears a greater significance than the actual values themselves.

The values for the back section are in every case slightly lower than those of the front section. The difference is, however, very small, and can scarcely be attributed to a separation.

The conclusion from these experiments seems to be that no separation, at least of the order expected, has occurred. It seems difficult to explain the failure of this method. There is very little doubt that the method would work if it could be applied to a gaseous system, and one must presumably therefore look for an explanation of its failure in the conditions characteristic of the liquid state.

In the first place the expression

$$V_f = V_0 + \frac{FEt}{M}$$

probably does not, at all accurately, express the motion of the ion between the events that we call collisions, as it presupposes a gradient of the field of force in the proximity of solvent molecules and ions very much greater than can reasonably be assumed. How great a difference a change in this assumption would introduce in the final result it is difficult to say, but it is possible that it might reduce the difference between the calculated mobilities considerably.

Furthermore, the expression

$$V_0 = V_f \left(\frac{M + m\left(\frac{1-\epsilon}{2}\right)}{M+m} \right)$$

may be considerably in error in representing the fraction of the initial velocity that remains after impact, as it involves the possibly false assumption that the velocities of molecules and ions, due to thermal agitation, can be assumed to cancel out, and that the velocities due to the electric field can be considered alone.

Neither of the above considerations could, however, lead to the conclusion that separation was impossible; for however small a fraction of the velocity before collision persists after it, accelerations (differing with the masses of the ions) must occur, and however short the path and time over which these accelerations take place, the average velocities of the two ions should never be quite the same.

If, on the other hand, there are factors which lead to variations of the velocities of individual ions independently of their masses, then separation might become indefinitely small.

There are several ways in which it may be suggested this variation could take place.

Firstly, the velocity might be reduced to zero through the ion becoming neutralized by combination with an ion of the opposite sign. In the case of $MgSO_4$ at half-normal concentration only 63·9 per cent. of the magnesium exists as ions, and in the case of half-normal KCl only 89·7 per cent. Thus, especially with magnesium, there would be a tendency for the faster ion to come to rest and to be overtaken by the slower one.

The same action would also take place if the jelly used in the experiments were capable of absorbing the ions. If this happened, the faster-moving ions would again be brought to rest and the slower catch them up.

If, lastly, the state of hydration (and consequently the mobilities) of the ions were to vary independently, a similar result would ensue. If there were a dynamic equilibrium of the kind,

$$Cl' + nH_2O \rightleftharpoons Cl'H_2O + (n-1)H_2O \rightleftharpoons Cl'2H_2O + (n-2)H_2O,$$

the mobility of the ion could have several distinct values.

The effect following from any of these three causes would be such as to make it useless to increase the distance, over which separation was attempted, above the average length individual ions could move without being affected by any of them. As this average distance would be small, it would be impossible to achieve any separation. It is probably due to a combination of all these causes that separation does not occur.

In conclusion, I should like to express my thanks to Prof. Lindemann, to Mr. A. C. Egerton, and to Mr. I. O. Griffith for constant help and advice during this work, and to the Scientific and Industrial Research Board for a grant whereby it has been possible to carry it out.

Summary.

(1) Formulæ are derived for the migration velocities of ions which differ in mass but which are otherwise identical.

(2) As a result of these formulæ, the possibility of separating isotopes by differences of migration velocities is discussed.

(3) Two series of experiments are described in which chlorine ions in the one case and magnesium ions in the other are made to migrate in a jelly of agar-agar under conditions judged to be suitable for separation.

(4) Atomic weight determinations, carried out by methods devised for the comparison of the products so obtained, indicate that no appreciable separation has been effected.

(5) The failure of the method to yield separation is discussed.

Clarendon Laboratory,
Oxford.
Sept. 1st, 1924.

XC. *Chemical Affinity and Electronic Structure.*—Part II. *The Polar Link.* *By* BERNARD HOWELL WILSDON [*].

IN a recent paper (Phil. Mag. Feb. 1925, p. 354) the author has developed a tentative theory of the energetics of the non-polar link on the basis of a quantum mechanism similar to that which has successfully explained the anomalous magnetic resolution of doublet and triplet spectral lines. It was there stated that an explanation of the polar type of combination followed in an analogous manner by the substitution of the Stark effect due to an electrostatic field for the magnetic field of the non-polar molecule. The fundamental argument is essentially the same in the two cases. It is assumed that a necessary condition for a stable molecular combination is that the frequencies of the valency orbits concerned shall be synchronized. If ν_1 and ν_2 represent the frequencies of the valency electrons of the combining atoms in their ground orbits, $h(\nu_1-\nu_2)$ represents a quantum of energy which is termed the available energy of accommodation, E_a. This energy is supposed to be responsible for the changes involved in the transfer of a valency electron or electrons from the positive to the negative atom, and for the potential energy of valency electrons and "trunk" in the field of the stripped positive ion. The change in frequency of the valency orbits produced under these conditions, multiplied by the unit of action, h, must then represent the change in kinetic energy. If we know the ratio of the kinetic to total energy in the field of the molecule, we can then calculate the total energy change which must be equal to the heat of formation. This ratio is known as a result of a theorem of Bohr (Phil. Mag. xxvi. p. 24, 1913). In a Coulomb field

$$E_{\text{kin}} = -\tfrac{1}{2}E_{\text{pot}},$$

so that

$$Q = \Delta W = \Delta E_{\text{kin}} + \Delta E_{\text{pot}} = -\Delta E_{\text{kin}}.$$

In order to determine the distribution of the available energy of accommodation in the molecule, it is necessary to make assumptions as to the changes in quantum numbers which will define the electrostatic moment of the charged elements of structure. Just as the magnetic moment of an electronic orbit is quantized in terms of the Bohr, the electrostatic moment must be a multiple or sub-multiple of the quantity $\frac{3h^2}{8\pi^2 meZ_e}$. Here Z_e is the effective atomic number, and the other symbols have their usual significance. If $\bar{x}$ represents the time mean displacement of an electron in the direction of a field F, its moment will be $\bar{x}e$, and its potential energy $\bar{x}e$F. As shown by Sommerfeld ('Atomic Structure,' Engl. trans. p. 311), if this is equated to the change in energy produced by the imposition of a field F as calculated by Schwarzschild and Epstein in explaining quantitatively the Stark effect, we have

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[*] Communicated by Dr. J. W. Nicholson, F.R.S.

$$\frac{3h^2}{8\pi^2 me}\cdot\frac{F}{Z_0}(n_1+n_2+n_3)(n_2-n_1)=e\bar{x}=\frac{CF}{Z_0}(n_1+n_2+n_3)(n_2-n_1), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is constant.

The quantum numbers here employed are the parabolic; $(n_1+n_2+n_3)$ is equal to the principal quantum number, and n_3 is the equatorial which defines the moment of momentum of the electron in the meridian plane of the molecule or atom. If $n_1=n_2$, the orbit is circular and the electron does not react to the imposed field. In the isolated atom the quantum numbers change only by whole numbers; in the molecule it appears necessary to admit of changes involving half numbers, as in the magnetic field. Arguments have been advanced by Mosharrafa (Proc. Roy. Soc. A, cv. p. 641, 1924) which indicate that such changes are also possible in the atom.

The change in potential energy resulting from the molecular combination of two atoms will be made up of three parts :—

(*a*) The work resulting from bringing the valency electron of the negative atom into the field of the positive. If q' represents the quantum factor assumed by this electron after adjustment, and F′ the field of the positive ion, the work will be

$$Cq'F'/Z', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,a)$$

where Z′ represents the effective atomic number of the negative atom.

(*b*) The work of bringing the valency electron of the positive ion into the field of the negative. This will be similarly

$$Cq''F''/Z''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,b)$$

(*c*) The work of approximating the two atomic trunks. We assume that by quantum changes in the moments of the two valency electrons a moment is conferred on the trunk of the negative ion such that it is equal to the sum of the decrements so caused. Thus, if the negative ion is characterized by a principal quantum index k, and each of the equatorial quantum numbers n_3' and n_3'' change by half units to k_3' and k_3'', the moment taken up by the trunk is assumed to be

$$k(n_3'-k_3'+n_3''-k_3'')\mathrm{C}=k\mathrm{C}.$$

The energy in the field F''' of the positive *ion* will thus be

$$k\mathrm{CF}'''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2\,c)$$

The sum of these energies will be equal to E_a, the available energy of accommodation.

The hypothesis we have made as to the frequency tuning of the two valency orbits of the negative ion gives a relation between the three fields appearing in the above equations. Let p, with the appropriate affix, represent a quantum factor characteristic of the uncombined atoms; then, on imposition of a field, the change in frequency of the orbit will be given by

$$\mathrm{F}_1=\frac{\Delta\nu\,.\,\mathrm{Z}_1}{\mathrm{C}p_1}; \quad \mathrm{F}_2=\frac{\Delta\nu\,.\,\mathrm{Z}_2}{\mathrm{C}p_2}; \quad \mathrm{F}_3=\frac{\Delta\nu\,.\,\mathrm{Z}_0}{\mathrm{C}p_1}. \quad . \qquad (3)$$

Substituting the above values for the fields in the sum of equations (2), we have

$$\mathrm{E}_a=-h\Delta\nu\left\{\frac{q_1}{p_1}+\frac{q_2}{p_2}+\frac{k\mathrm{Z}_0}{p_1}\right\}. \quad . \quad . \quad . \qquad (4)$$

Whence, since $\mathrm{Q}=-h\Delta\nu$, we have

$$\mathrm{Q}=-h\Delta\nu=\frac{\mathrm{E}_a}{\left\{\frac{q_1}{p_1}+\frac{q_2}{p_2}+\frac{k\mathrm{Z}_0}{p_1}\right\}}=\frac{\mathrm{E}_a}{\mathrm{D}}. \quad . \quad . \qquad (5)$$

In this formula it will be noted that all the effective atomic numbers, except that which refers to the negative ion, have cancelled out. The value of the remaining constant is taken as 4·195; this corresponds with the effective charge of a nucleus with 7 positive charges corrected for a screen of 8 electrons. For 8 electrons the Sommerfeld screening number is equal to 2·805; the effective atomic number of a halogen ion is thus 7−2·805 or 4·195.

In order to apply the above relations to the calculation of heats of formation of polar compounds, we must first investigate the form of the quantum factors p and q. According to the theory of the Stark effect, the change in energy of an orbit under the influence of a field F is given by equation (1) above. For a change in free energy corresponding with emission or absorption of a spectral line, the change in frequency must depend upon the difference of two terms—*i. e.*, the change in kinetic energy must be given by

$$h\Delta\nu=\frac{h\mathrm{CF}}{\mathrm{Z}}\{(n_2-n_1)(n_1+n_2+n_3)-(k_2-k_1)(k_1+k_2+k_3)\}$$

$$=\frac{h\mathrm{CF}}{p}, \quad . \quad . \quad . \quad (6)$$

where the n's refer to the final state and the k's to the initial.

There are two possible types of quantum jump corresponding with this emission or absorption. In the first the equatorial quantum number n_3 remains unaltered. This, according to the theory of the Stark effect, corresponds with a parallel polarized light wave; it is one of the great triumphs of the theory that this prediction is constantly verified by spectral evidence. In molecular combination it will then be justifiable to assume that a quantum change which will produce in the free atom a parallel polarized ray will result in an orientation of the orbit which is parallel with the field of the second atom.

In the second type the equatorial quantum number jumps by one unit, so that $n_3=k\pm1$. The light is then polarized in a direction perpendicular to the field, and we shall consequently assume that the orbit is arranged in a plane at right angles to the field of the second atom. If these suppositions are true, we may expect two distinct types of polar compounds. Experimental results appear to support the prediction; it will be seen that the distinction arranges elements into classes which correspond with the A and B subgroups of the periodic table.

If the quantum factor p of the valency orbit of the atom is not equal to zero, *i. e.* if $(n_2-n_1)(n_1+n_2+n_3)\neq0$, the change in frequency resulting by increasing the field from zero to F will be given by

$$\Delta\nu=\frac{\mathrm{CF}}{\mathrm{Z}}\cdot p-0=\frac{\mathrm{CF}}{\mathrm{Z}}(n_2-n_1)(n_1+n_2+n_3). \quad . \quad (7)$$

This corresponds with parallel orientation, since n_3 the equatorial quantum number has not changed. This condition appears to be characteristic of the A group of the periodic table—*i. e.*, those elements which in the ionic form are surrounded with a complete valency shell of eight electrons. If the electronic orbit has zero moment, *i. e.* if $p=0$, no change in frequency can result on application of the field. The emission must now take place in two steps: (1) activation involving increase by one unit in the quantum sum, followed by (2) resumption of an orbit characterized by the original quantum sum. The process (1) must, according to the theory of the Stark effect, involve also change in the parabolic quantum numbers, as otherwise no change in energy would result. The resulting change in frequency will correspond with the difference in the energies of these states. If the original condition is defined by the quantum factor $(n_1+n_2+n_3)(n_2-n_1)$ and $n_2=n_1$, while the second state is $(k_1+k_2+k_3)(k_2-k_1)$ where $k_1+k_2+k_3=n_1+n_2+n_3+1$, the activated atom changes to $(k_1+k_2+k_3-1)(k_2-k_1)$, whence the total change becomes (k_2-k_1). $\Delta\nu$ will then be given by

$$\Delta\nu=\frac{\mathrm{CF}}{\mathrm{Z}}(k_2-k_1).$$

Among the elements which fall into this class we must place hydrogen, since it must have the constitution 1(00), where the symbol indicates the quantum numbers $n_3(n_1n_2)$. In the halogen elements the equatorial quantum number is always 2, so the constitution of fluorine, whose quantum sum is also 2, must be 2(00). Fluorine will therefore fall into the same class. Copper, silver, gold, zinc, cadmium, and mercury are similarly assumed to have constitutions with zero moment.

The application of these relations is first made to monovalent elements of class A—viz., the alkali halides with the exception of the fluorides. In Table I. are given, in columns 2 and 4, the p constitutions assumed (the atomic quantum factors); columns 3 and 5 give the q states (the molecular quantum factors). These are obtained by change of the equatorial quantum number by $-\frac{1}{2}$ and a change in the parabolic quantum numbers compatible with the constancy of the quantum sum. D in column 6 then represents the denominator occurring in equation (5). It is to be noted that in this type of combination the principal quantum number cancels out from the denominator and numerator.

TABLE I.

Heats of Formation of Alkali Halides.

1.	2. *p*.	3. *q*.	4. *p*.	5. *q*.	6. D.	7. E_a.	8. Q calc.	9. Q found.
LiCl	1(01)	½(0,3/2)	2(01)	3/2(0,3/2)	7·195	682·6	94·88	93·8
LiBr	,,	,,	2(02)	3/2(0,5/2)	4·348	349·9	80·48	79·96
LiI	,,	,,	2(03)	3/2(0,7/2)	3·064	196·1	64·0	61·21
NaCl	1(02)	3/2(½,2)	2(01)	3/2(0,5/2)	7·445	725·8	97·5	97·69, 97·9
,, ...	,,	3/2(0,5/2)	,,	3/2(0,3/2)	6·915	...	104·5*	...
NaBr	,,	,,	2(02)	3/2(0,5/2)	4·598	393·0	85·48	85·71, 86·1
NaI	,,	,,	2(03)	3/2(0,5/2)	3·482	239·2	68·7	69·08
KCl	1(03)	½(0,7/2)	2(01)	3/2(0,3/2)	6·861	741·4	108·0	105·61, 105·7
KBr	,,	½(0,7/2)	2(02)	3/2(0,5/2)	4·515	427·4	94·66	95·31, 95·6
KI	,,	½(½,3)	2(03)	3/2(½,3)	3·065	254·3	82·98	80·13

In column 7, E_a gives the available energy of accommodation calculated in kilogram calories per molecule according to the equation

$$E_a = A\left(\frac{Z_1^2}{n_1^2} - \frac{Z_2^2}{n_2^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here $A = \frac{hR_0L}{J}$; h is the constant of action, R the Rydberg constant, L Avogadro's number, and J the mechanical equivalent of heat, whence substituting the appropriate values $A = 310{\cdot}2$ Cal. Column 9 gives the experimental values of the heats of formation; these are taken from Landolt and Börnstein's Tables (5th edition); where divergent values are recorded, both are given. Column 8 gives the calculated heats of formation—*i. e.*, the quotient of E_a by D.

An example will make the method of calculation clear. The chlorine atom, distinguished by the asterisk in the above table, has, in the p state, the constitution 2(01); $p_2 = (n_1 + n_2 + n_3)(n_2 - n_1)$ is thus equal to 3(1). By change of $\frac{1}{2}$ unit in the equatorial quantum number the molecular quantum factor q_2 becomes 3(3/2). Of the available accommodation energy, the impulse taken up by the valency electron of the chlorine atom is thus $\frac{3(3/2)}{3(1)} \,.\, h\Delta\nu$. Similarly in lithium chloride, the lithium atom has for the p state the factor 2(1) and in the q state 2(3/2), so the impulse taken up by this orbit is $\frac{2(3/2)}{2(1)} \,.\, h\Delta\nu$. The impulse taken up by the trunk is then $\frac{3(\frac{1}{2}+\frac{1}{2})}{3(1)} \,.\, 4{\cdot}195 = \frac{kZ_0\Delta\nu}{p}$, since the field F_3 is defined by the quantum factor of the halogen ion for which $p_2 = 3(1)$. The sum of the impulses is $7{\cdot}195\ h\Delta\nu$; E_a is given according to equation (8) by

$$310{\cdot}2\left(\frac{22{\cdot}04}{9} - \frac{1}{4}\right) = 682{\cdot}6 \text{ Cal.},$$

in which 22·04 is the square of the effective atomic number of an element of the 7th column of the periodic table, 1 the effective atomic number of the alkali, and 9 and 2 the squares of the principal quantum numbers of the chlorine and lithium atoms respectively. The quotient E_a/D 94·88 gives the theoretical heat of formation; the experimental value found is 93·8 Cal.

With sodium bromide $p_1=3(2)$ changes to $3(5/2)$, $p_2=4(2)$ changes to $q_2=4(5/2)$, so that D becomes

$$\frac{3(5/2)}{3(2)}+\frac{4(5/2)}{4(2)}+\frac{4\,.\,4{\cdot}195}{4(2)}=4{\cdot}598,$$

whence $Q=\frac{393{\cdot}0}{4{\cdot}598}=85{\cdot}48$: found 85·71 and 86·1.

With lithium bromide, sodium iodide, and potassium iodide the closest agreements with experimental values are obtained by assuming that the k_1 parabolic quantum number takes up the amount of $\frac{1}{2}$, available by decrease of the equatorial quantum number. This makes the quantum factor decrease, instead of increasing as appears usual. With sodium iodide, if we assume that the k_1 quantum number remains zero, instead of the values given in the table we shall have $D=5/2\,.\,1/2+7/2\,.\,1/3+4{\cdot}195/3=3{\cdot}765$, so that Q becomes 63·52 instead of 68·7. It will be found similarly that in the other cases the theoretical value is not altered by more than about 10 per cent. by disallowing change of the k quantum number. It is to be noted that there is no apparent reason why this change should be disallowed beyond the natural tendency to require that the distribution of impulse in apparently similar molecules should be the same. In the case of sodium chloride, good agreement is obtained by supposing that the k_2 quantum number of the halogen orbit increases by 3/2, while that of the alkali decreases by $\frac{1}{2}$. The total change is thus still unity, as our hypothesis demands. The latitude which results from the selection of a quantum factor from among several permissible values is admittedly the most unsatisfactory feature of the theory, and the accuracy of the experimental data by which it is tested is at present not sufficiently great to enable reliance to be placed on agreement between theoretical and experimental values in deciding on what quantum jumps are permissible. Moreover, it must be remembered that the introduction of the effective atomic number into our calculations can give it no more than the significance of an approximation. On the other hand, the fact that the heats of formation calculated according to different permissible quantum jumps do not greatly alter in magnitude leads to greater confidence, especially if it is recognized that it is scarcely probable that the molecule when formed is characterized by an unique electronic configuration. In fact, it seems very probable that observed heats of formation will be affected by a probability factor, and represent only a statistical average of possible changes.

It may eventually be possible to estimate these probabilities in the manner which has proved so successful in determining the intensities of electrically resolved spectral lines by the Bohr principle of correspondence.

We may now consider the data for di-atomic molecules which, on account of the electronic constitution it is necessary to assume for one of the atoms in its unexcited state, we class as type B compounds. This class will include hydrogen compounds, since in the unexcited state its quantum factor cannot be other than 1(00), and fluorine which must certainly be written 2(00). For the quantum states of the elements of the B subgroups of the first and second columns of the periodic table, it is not possible to decide with certainty. There can be no doubt, however, that these elements are assigned to their right class, since the occurrence of the principal quantum number of the negative atom in the numerator only, largely diminishes the magnitude of the heat of formation calculated according to the hypotheses we have adopted. Table II. gives the p and q values which it is necessary to assume to obtain the best agreement with the experimental values. The $p \rightarrow q$ quantum jumps, in the case of the elements of higher principal quantum number, are not always simple changes by $\frac{1}{2}$ units; it appears that the equatorial numbers may change by whole numbers in addition to the $\frac{1}{2}$ unit which seems to be a constant feature of the molecular quantum number. The regularities observed in the quantum factors assumed are sufficiently striking to remove suspicions that agreement between experimental and calculated values is merely accidental.

In each series the quantum factor for a particular element is a constant term, with the exception of silver bromide, where another permissible change gives better agreement. The term contributed by the halogen element appears to be constant throughout, except in the halogen hydracids. Hydrogen fluoride and silver fluoride are decidedly abnormal, as might have been expected, since both atoms in the undisturbed state have zero moment in the field. The chemical properties of hydrogen fluoride in particular are undoubtedly against its formulation as a polar compound. If equilibrium exists between the two forms, it must be preponderatingly in favour of the non-polar constitution. It is interesting to note that in both these abnormal cases the calculated heat of formation is very approximately one-third of that observed. This factor might be justified, as proposed in Part I. of this paper (*loc. cit.*), by supposing that the ratio of kinetic to

TABLE II.

Heats of Formation of Type B Compounds.

	p_{10}.	p_1.	q_1.	p_{20}.	p_2.	q_2.	D.	E_a.	$E_a/D=Q$.	Q found.
HCl	1(00)	1(01)	1/2(1/2,1)	2(01)	...	1/2(0,5/2)	20·59	449·7	21·85	22·0 (26·0 at 2000°)
HBr..............	,,	,,	,,	2(02)	...	3/2(0,5/2)	13·89	114·12	8·22	8·44, 8·6
HI	,,	,,	,,	2(03)	...	5/2(0,5/2)	11·66	−73·2	−6·28	−6·44, −6·4
HF	,,	,,	,,	2(00)	2(01)	1/2(0,3/2)	11·89	1399·2	117·7	38·5
LiF	...	1(01)	1/2(0,3/2)	,,	,,	,,	14·39	1632·0	113·4	114·3, 115·8
NaF..............	...	2(01)	3/2(0,3/2)	,,	,,	,,	15·89	1674·8	105·4	102·6, 109·2
KF	...	2(02)	5/2(0,3/2)	,,	,,	,,	14·39	1691·8	117·6	118·1
CuCl	2(11)	1(12)	1/2(1,5/2)	2(01)	...	3/2(0,3/2)	22·09	740·6	33·53	32·87, 35·4
CuBr	,,	,,	,,	2(02)	...	5/2(0,3/2)	17·39	408·2	23·47	24·98
CuI	,,	,,	,,	2(03)	...	7/2(0,3/2)	15·49	254·3	16·42	16·26, 16·9
AgF..............	1(22)	1(13)	3/2(0,7/2)	2(00)	2(01)	1/2(0,3/2)	17·64	1698·0	84·30	23·2
AgCl	,,	,,	,,	2(01)	...	3/2(0,3/2)	25·84	747·6	28·94	29·38, 29·0, 29·94
AgBr	,,	,,	5/2(0,5/2)	2(02)	...	5/2(0,3/2)	17·64	415·0	23·52	22·7, 23·4
AgI	,,	,,	3/2(0,7/2)	2(03)	...	7/2(0,3/2)	18·24	261·3	14·32	13·80, 14·2, 14·99
HgCl	1(33)	2(14)	3/2(3/2,4)	2(01)	...	3/2(0,3/2)	22·92	741·4	32·35	31·3, 31·32, 32·605
HgBr	,,	,,	,,	2(02)	...	5/2(0,3/2)	17·22	407·9	23·69	24·5, 25·475
HgI	,,	,,	,,	2(03)	...	7/2(0,3/2)	15·33	254·3	16·59	14·2, 15·55

total energy change is characteristic of a magnetic field in which $Q=1/3\ E_{\text{kin}}$.

As an example of the calculation, we may take the case of silver bromide; the silver atom by excitation is supposed to undergo the jumps $1(22)\rightarrow 2(13)\rightarrow 1(13)$, so that F_1 is given by $\Delta\nu=\frac{CF_1}{Z_1}.\,(3-1)$. The molecular quantum factor, by the $\frac{1}{2}$ unit change, then becomes $5(7/2-1)$ or, what amounts to the same thing, $5(5/2-0)$, so that q_1/p_1 becomes $\frac{5(5/2)}{2}$.

The bromine atom on combination is assumed to undergo the jump $2(02)\rightarrow 3/2(\frac{1}{2},2)$ or $5/2(0,3/2)$, so that $q_2/p_2=\frac{3(3/2)}{2}$. The trunk takes up the impulse $4/2\,.\,Z_0 h\Delta\nu$, so that the total energy change becomes

$$E_a=415{\cdot}0=\left\{\frac{5(5/2)}{2}+\frac{4(3/2)}{2}+4/2\,.\,4{\cdot}195\right\}.\,h\Delta\nu$$
$$=17{\cdot}64\,h\Delta\nu,$$

whence $Q=23{\cdot}52$: found $22{\cdot}7$ and $23{\cdot}4$ Cal., between which the theoretical value falls.

In polyatomic molecules, negative terms must enter into the denominator D on account of the energy of strain between similarly charged ions. Thus, for instance, in the case of calcium chloride the available energy of accommodation must also comprise the negative work necessary for bringing the two chlorine ions into proximity. It is not at present advisable to attempt to calculate these heats until more experience has been gained of the simple diatomic compounds. It is interesting to note, however, that the same general relations between elements of the A and B subgroups are evident as were observed before. The denominator D for the B subgroup is always much greater than that of the A subgroup. With increasing values of the principal quantum number the denominator for the halides of group B elements decreases much less with increase in atomic weight of the halide than in the A group, where the ratios are approximately of the same order. This must undoubtedly be due to the constant term contributed by the positive ion which is proportional to its principal quantum number; the denominator as a whole

TABLE III.

Heats of Formation of the Halides of Divalent Elements.

Principal quantum no.	E_a.	GROUP A.			GROUP B.		
			Q found.	D.		Q found.	D.
2 …………	522·5	$BeCl_2$	155·0	3·37	…	…	…
3 …………	654·4	$MgCl_2$	151·01	4·33	…	…	…
	322·0	$MgBr_2$	121·7	2·65	…	…	…
	168·2	MgI_2	84·8	1·98	…	…	…
4 …………	700·8	$CaCl_2$	183·89 190·3	3·75	$ZnCl_2$	97·21 97·4	7·20
	368·2	$CaBr_2$	154·92	2·38	$ZnBr_2$	75·93 76·0	4·85
	214·5	CaI_2	149·01	1·44	ZnI_2	49·231	4·36
5 …………	721·8	$SrCl_2$	184·56 184·7	3·91	$CdCl_2$	93·24	7·74
	389·3	$SrBr_2$	157·70 158·1	2·47	$CdBr_2$	75·20 76·3	5·14
	235·5	SrI_2	122·9	1·92	CdI_2	48·82	4·82
6 …………	733·6	$BaCl_2$	196·88 197·1	3·72	…	…	…
	401·0	$BaBr_2$	172·1 172·4	2·33	…	…	…
	247·3	BaI_2	136·1	1·82	…	…	…
7 …………	741·4	…	…	…	$HgCl_2$	53·3 54·49	13·60
	407·9	…	…	…	$HgBr_2$	40·5 40·6 41·88	9·73
	254·3	…	…	…	HgI_2	25·2	9·81

thus becomes more nearly constant. This can be seen from an inspection of Table III., where the quotients of E by the mean value of the experimental heats of formation are compared.

Simla,
October 1924.

XCI. *The Motion of an Electric Charge.* By ARTHUR BRAMLEY, *Ph.D., Fellow in Physics, Princeton University* *.

ANY discussion of the motion of electric charges must be based on the fundamental laws of electrodynamics as developed into their final state by Maxwell. The consideration of the relation of the charge to the electric and magnetic field is based on experimental laws:

$$\int \mathrm{H}x\,dx+\mathrm{H}y\,dy+\mathrm{H}z\,dz=\iint\left(\rho v+\frac{d\mathrm{E}}{dt}\right)_n d\mathrm{S}, \quad . \quad \text{(i.)}$$

where the line integral is taken over any particular closed curve, and the surface integral over any surface bounded by this curve, where H = magnetic field, E = electric field, ρv = electric flux through the surface at any point, and n denotes the normal component

$$\int \mathrm{E}x\,dx+\mathrm{E}y\,dy+\mathrm{E}z\,dz=-\iint\left(\frac{d\mathrm{H}}{dt}\right)_n d\mathrm{S}. \quad . \quad . \quad \text{(ii.)}$$

If we know ρv as a continuous function of position at any particular instant t, we can write the above equations in the well-known form

$$\left.\begin{aligned}\rho u+\frac{\partial \mathrm{E}_x}{\partial t}&=\mathrm{curl}_x\mathrm{H},\\ -\frac{\partial \mathrm{H}_x}{\partial t}&=\mathrm{curl}_x\mathrm{E},\end{aligned}\right\}\text{etc.,} \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where u = the component along the x-axis.

Now, as Einstein has pointed out (Berlin Academy, January 1924), these equations define a relation between the field and the charge at any given instant, but do not correlate the different images of the electromagnetic phenomena at any instant t with that at any other instant t'.

Let us consider a four-dimensional manifold (x, y, z, t) where x, y, z are the space coordinates and t the time coordinate, and where

$$ds^2=dx^2+dy^2+dz^2-dt^2,$$
$$c^2=1,$$

as in special relativity.

Then the fundamental integrals and hence Maxwell's equation refer to any space-like variety

$$d\bar{s}^2=dx^2+dy^2+dz^2,$$

obtained by taking a section perpendicular to the time-axis.

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* Communicated by the Author.

The electric flux ρv will be a function of position in any one variety

$$t=t_0,$$
$$(\rho v)=f(x, y, z),$$

and hence can be expressed as a function of position in the four-dimensional space

$$(\rho v)=f(x, y, z, t).$$

Now, if there are no point charges in the field, *i. e.* singularities, we can expand the flux as a function of the time, *e. g.*,

$$(\rho u)=(\rho u)_0+(\rho u)_1 t+(\rho u)_2 t^2+\ldots\ldots,$$

where $(\rho u)_0$, $(\rho u)_1$, and $(\rho u)_2$, etc.,

are functions of (x, y, z).

Further, we can expand E and H as a power series in t,

$$E=E_0+E_1 t+E_2 t^2+E_3 t^3+\ldots.,$$
$$H=H_0+H_1 t+H_2 t^2+H_3 t^3+\ldots.,$$

where E_0, H_0, E_1, H_1, etc., are functions of x, y, and z only, and where E and H represent any one of the three components E_x, H_x, etc., the distribution of charge and velocity being of such a nature that the series are convergent.

Taking the case of motion along the x-axis, we get, by substituting in Maxwell's equation,

$$\begin{aligned}&(\rho u)_0+(\rho u)_1 t+(\rho u)_2 t^2+\ \ldots.\\&+E_1+2E_2 t+3E_3 t^2+\ \ldots.\\&=\text{curl } H_0+\text{curl } H_1 . t+\text{curl } H_2 . t^2+\ \ldots.\end{aligned}$$

Since these equations must be valid for all values of t, we have

$$\begin{aligned}&(\rho u)_0+E_1=\text{curl } H_0,\\&(\rho u)_1+2E_2=\text{curl } H_1,\\&(\rho u)_n+(n+1)E_{n+1}=\text{curl } H_n,\end{aligned}$$

where

$$(\rho u)=(\rho u)_0+(\rho u)_1 t+\ \ldots.$$

Similarly, for the second set of Maxwell's equations,

$$\begin{aligned}H_1&=\text{curl } E_0,\\2H_2&=\text{curl } E_1,\\(n+1)H_{n+1}&=\text{curl } E_n.\end{aligned}$$

For points where $\rho=0$ for all values of t,

$$E_1=\operatorname{curl} H_0,$$

$$E_{2n}=\frac{\pm}{\underline{|2n}}\nabla_1^2\ldots\ldots\nabla_n^2 E_0,$$

$$E_{2n-1}=\frac{\mp}{\underline{|2n-1}}\nabla_1^2\ldots\ldots\nabla_{n-1}^2 E_1,$$

and a similar set of equations for H. These equations allow us to determine all the subsequent coefficients from the knowledge of E_0 and H_0, E_0 and H_0 being the values of the two field intensities at a particular instant when

$$t=0.$$

These equations (iii.) are subject, however, to certain kinematic conditions determined by the nature and motion of the electric charges. In the classical method of solution of Maxwell's equations developed by Kirchhoff, the magnetic and electric forces are given by the equations

$$H=\operatorname{rot}\psi,$$

$$E=-\frac{\partial\psi}{\partial t}-\operatorname{grad}\phi,$$

where

$$\phi=\frac{1}{4\pi}\iiint\frac{\rho'}{r}\,dx\,dy\,dz,$$

$$\psi=\frac{1}{4\pi}\iiint\frac{(\rho v)'}{r}\,dx\,dy\,dz,$$

where the dash denotes that in carrying out the integrations the values of ρ and ρv, respectively, at the time $t=-r$ previous to that for which the integrals are being evaluated, have to be substituted.

Suppose that the electric flux (ρv) is moving along the x-axis, being defined by the equation of propagation

$$\rho u=f\{x-at^n\},$$

then

$$(\rho u)'=f\{x-a(t-r)^n\};$$

whence

$$\left[\frac{\partial^m(\rho u')}{\partial t^m}\right]_{t-r=0}=0, \qquad m<n,$$

where

$$\left[\frac{\partial^n(\rho u)'}{\partial t^n}\right]_{t-r=0}=f'(x)=\frac{\partial f}{\partial\{x-a(t-r)^n\}}.$$

In the case where the density ρ is different from zero only at and in the neighbourhood of a point, the equation

$$(\rho u)=f\{x-at^n\}$$

defines the motion of the point charge according to the equation

$$x-at^n=\text{const.}=\mathrm{A};$$

for if we consider the motion of the maximum value of the flux, *i. e.* the flux at the position of the charge, we see that it is defined by

$$(\rho u)_{\text{max.}}=f(\mathrm{A}),$$

where

$$\mathrm{A}=x-at^n,$$

being the value for which $f(y)$ is a maximum.

If $n=2$, the motion of the charge is uniformly accelerated.

If we consider the motion of a charge whose density is different from zero only at and in the neighbourhood of a certain point, fixed or moving, then from the definition of H we see that since in this case we can regard (ρu) as a function of the form,

$$\rho u=(\rho u)_0+(\rho u)_n t^n+\,..$$

i. e.,

$$(\rho u)_i=0, \qquad i=1\,....\,x-1,$$

so that the first $n-1$ time-derivatives of the magnetic intensity are zero along the light-cone

$$(x-x')^2+(y-y')^2+(z-z')^2=t^2$$

for any position (x', y', z', t') of the electric charge. As the charge moves along, the conic surface will describe a continuous parametric family of surfaces over which the above derivatives are zero. Since the derivatives which are continuous functions of position are zero throughout the column generated by the cone, they must be zero for all points in space. Hence

$$\frac{\partial^m \mathrm{H}}{\partial t^m}=0, \qquad m<n,$$

or

$$\mathrm{H}_i=0, \quad i=1\,....\,n-1.$$

(See note p. 922.)

For the case where the charge is stationary or moving with uniform rectilinear motion, the expansions are not subject to any kinematic conditions. Let us therefore consider the case of uniform accelerated motion,

then
$$\rho u = f(x - at^2)\,;$$
$$H_1 = 0\,;$$
i. e.,
$$\text{curl } E_0 = 0.$$

Let us assume that initially the solution has the form

$$E_{0x} = \frac{ex}{r^3} + \chi_x, \quad E_{0y} = \frac{ey}{r^3} + \chi_y, \quad E_{0z} = \frac{ez}{r^3} + \chi_z,$$

where χ is an arbitrary function which has to be determined. Since

$$\text{curl } E_0 = 0$$

and

$$\text{div. } E_0 = 0 \quad \text{where} \quad \rho = 0,$$

we have that

$$\chi_x = \frac{\partial \chi'}{\partial x}, \quad \chi_y = \frac{\partial \chi'}{\partial y}, \quad \chi_z = \frac{\partial \chi'}{\partial z},$$

where

$$\Delta^2 \chi' = 0.$$

If we consider the radiation from this system defined by Poynting's vector,

$$\Pi_x = E_{0y} H_{0z} - E_{0z} H_{0y},$$
$$\Pi_y = E_{0z} H_{0x} - E_{0x} H_{0z},$$
$$\Pi_z = E_{0x} H_{0y} - E_{0y} H_{0x},$$

since the terms in higher powers of t contain higher powers of $\frac{1}{r}$, being derivatives of H_0 and E_0 respectively, we see that the radiation must be zero, since E_0 is derived from a potential function, *i. e.*,

$$E_{0x} = \frac{\partial V}{\partial x}, \quad E_{0y} = \frac{\partial V}{\partial y}, \quad E_{0z} = \frac{\partial V}{\partial z};$$

so that the system in uniform accelerating motion can never radiate energy when obeying the classical electrodynamical laws.

From the above discussion we see that the classical radiation field developed from Kirchhoff's solution of Maxwell's equations can only be regarded as a fictitious solution which contains no energy; in the gravitational field several examples of fictitious fields have been pointed out by

Eddington, while Bohr has developed the consequences of the idea applied to electromagnetic theory *.

Let us next consider the motion of an electric charge obeying the familiar laws of electrodynamics, and hence radiating no energy.

The equation of motion of the charge e in the Riemannian space

$$ds^2=g_{ij}\,dx^i\,dx^j$$

is

$$\frac{ds}{dt}\left(m\cdot\frac{dt}{ds}\right)\left[\frac{d^2x^2}{ds^2}+\Gamma^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right]=F'^2_\alpha\frac{dx^\alpha}{dt}, \quad . \quad (A)$$

where $\Gamma^2_{\alpha\beta}$ is the Christoffel symbol and F'^2_α the component of force acting on the charge.

Since

$$\frac{ds}{dt}=\frac{ds}{dx^4},$$

we have

$$\frac{d^2x^2}{ds^2}+\Gamma^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}=\frac{F'^2_\alpha}{m}\frac{dx^\alpha}{ds}\cdot\frac{ds}{dx^4}.$$

Let

$$\frac{dx^i}{ds}=\phi^i\cdot\dot{x}^4,\quad \dot{x}^i=\frac{dx^2}{ds},\quad i=1\ldots\ldots4,$$

$$\phi^4\equiv1\,;$$

then we get

$$\phi^i\cdot\ddot{x}^4+\frac{\partial\phi^i}{\partial x^\alpha}\,\phi^\alpha(\dot{x}^4)^2+\Gamma^i_{\alpha\beta}\phi^\alpha\phi^\beta(\dot{x}^4)^2=\frac{F'^i_\alpha}{m}\phi^\alpha,$$

or

$$\ddot{x}^4\phi^i+(\dot{x}^4)^2\left\{\frac{\partial\phi^i}{\partial x^\alpha}\phi^\alpha+\Gamma^i_{\alpha\beta}\phi^\alpha\phi^\beta\right\}-\frac{F'^i_\alpha}{m}\phi^\alpha=0,$$

$$i=1\ldots\ldots4.$$

These four equations allow us to solve for the four unknowns

$$\dot{x}^4,\quad \phi',\quad \phi^2,\quad \text{and}\quad \phi^3.$$

Knowing this solution, we can write our equation in the form

$$\frac{d^2x^i}{ds^2}+\left\{\Gamma^i_{\alpha\beta}-\frac{F'^i_\mu\phi^\mu}{m}g_{\alpha\beta}\right\}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}=0,$$

or

$$\frac{d^2x^i}{ds^2}+G^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}=0, \quad . \quad . \quad . \quad . \quad (B)$$

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* Bohr, Kramer, and Slater, Phil. Mag. xlvii. p. 785 (1924).

where

$$G^i_{\alpha\beta}=\Gamma^i_{\alpha\beta}-\frac{F'^i_{\mu}\phi^\mu}{m}g_{\alpha\beta}$$

for

$$1=g_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}.$$

The equation (A) gives

$$\frac{dx^i}{ds}=\psi^i(s),$$

where s is the parameter along the path.

But $s=\chi(x)$, a function of position on the curve, allows us to write

$$\frac{dx^i}{ds}=f'(x);$$

so that ϕ^i is a function of $(x^1 \ldots . x^4)$ only.

Thus, in equation (B) the $G^i_{\alpha\beta}$ is a function, not only of position but also of the particular path. This leads to a more generalized geometry than the geometry of paths, considered by Eisenhart and Veblen, in which $\Gamma^2_{\alpha\beta}$ is a function of position only. Whence we are led to a result analogous to the fundamental assumption (L. P. Eisenhart, Nat. Academy, June 1923) that the motion of electrons manifests itself in paths in a space-time continuum of four dimensions.

We shall not consider an application of the ideas involved above to the case of a charge moving geodesically (in a particular path) in the space with linear element

$$-ds^2=\left(1-\frac{2e}{r}\right)^{-1}dr^2+r^2\,d\theta^2+r^2\sin^2\theta\,d\phi^2-\left(1-\frac{2e}{r}\right)dt^2,$$

where e = a constant depending on the charge at the origin of coordinates which produces the field.

If we wish to make the electron stationary in the field at any point, we must apply an external force to it which will become equal and opposite to the fictitious field due to the metric when the electron becomes at rest.

The equation representing the stationary electron at any point in space is therefore

$$g_{ij}\left(\frac{d^2x^j}{ds^2}+G^j_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right)=\psi_i,$$

where

$$\psi_i = -\mathrm{F}_{ik}\mathrm{J}^k/_\beta,$$

$$\beta = \frac{dt}{ds},$$

where F_{ik} represents the forces due to the field of the metric.

Since

$$\frac{dx'}{ds} = \frac{dx^2}{ds} = \frac{dx^3}{ds} = 0 \quad \text{and} \quad \frac{dx^4}{ds} = 1$$

when the electron is stationary, we get

$$g_{ij}\mathrm{G}^j_{44} = \psi_i = \mathrm{F}_{ik}\mathrm{J}^k/_\beta.$$

The only equation not zero is

$$g_{11}\mathrm{G}'_{44} = \psi_1 = -\mathrm{F}_{14}(-\epsilon)$$

or

$$\mathrm{G}'_{44} = \left(\frac{2e}{\epsilon}\right)\frac{-\epsilon}{r} = \epsilon\mathrm{F}_{14}.$$

Thus

$$2e = \epsilon^2,$$

where

$$\epsilon = \text{charge on nucleus} = \text{charge on electron}.$$

Thus the law of force is the well-known inverse square law; *i.e.*, the fictitious forces due to the metric make the path of the charge (electron here considered) equivalent to that of a charge in flat space under the influence of Coulomb's law.

The same problem has been considered by the author (Proc. Nat. Acad., Aug. 1923, "Motion of an Electric Particle in a Riemann Space") for an infinitesimal particle where the same conclusions were reached regarding the motion.

In this section we have considered the motion of any electric charge without radiation of energy, and find that we can express the equations of motion in the form

$$\frac{d^2x^2}{ds^2} + \mathrm{G}^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0,$$

where $\mathrm{G}^2_{\alpha\beta}$ depends not only on a point function, but also *on the character of the path of the charge.* If we can write the energy tensor in the form of squares, then

$$ds^2 = g_{11}dx_1^2 + g_{22}dx_2^2 + g_{33}dx_3^2 + g_{44}dx_4^2,$$

where

$$g_{ii} = g_{ii}(x^1, x^2, x^3, x^4, \alpha_{ii}),$$

where α_{ii} depends on the trajectory, the α's being different for different paths. These parameters, the α's, are closely connected with the quantum numbers which serve to define the equations of motion when written in integral form.

Lastly, the above analysis is applied to the simple linear element

$$-ds^2 = \left(1-\frac{2e}{r}\right)^{-1} dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta \, d\phi^2 - \left(1-\frac{2e}{r}\right) dt^2,$$

where the α's have been left arbitrary, since they can only modify the form of the function representing the force by a constant multiplier.

We are next going to consider the most general motion of a charge radiating no energy but under the influence of Maxwellian forces, and also a resisting force proportional to the velocity *.

The equation of motion is, therefore,

$$\ddot{x}^2 + \Gamma^2_{\alpha\beta} \dot{x}^\alpha \dot{x}^\beta - \mathrm{G} \dot{x}^2 = 0,$$

where G is a scalar proportionality factor.

The scalar G can, however, be written in the form

$$\mathrm{G} = \mathrm{G}_{\alpha\beta} \dot{x}^\alpha \dot{x}^\beta,$$

where $\mathrm{G}_{\alpha\beta}$ is a function of position only.

Let us then consider a set of paths defined by the n equations

$$\ddot{x}^i + \Gamma^i_{\alpha\beta} \dot{x}^\alpha \dot{x}^\beta - \dot{x}^i \, \mathrm{G}_{\alpha\beta} \dot{x}^\alpha \dot{x}^\beta = 0, \quad . \quad . \quad . \quad \text{(I.)}$$

where $\Gamma^2_{\alpha\beta}$ and $\mathrm{G}_{\alpha\beta}$ are tensor functions of position only.

The condition that the equation (I.) has a solution of the form

$$e^{\int \phi_\alpha dx_\alpha} g_{u\beta} \dot{x}^\alpha \dot{x}^\beta = \text{const.} \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

is that

$$[grs/t + 2g\alpha r \, \mathrm{G}st \, \dot{x}^\alpha + \phi r \, gst] \, \dot{x} \, \dot{x}^s \, \dot{x}^t \equiv 0.$$

A particular solution of this is

$$\begin{aligned} \mathrm{G}rs/t \, \dot{x}^r \dot{x}^s \dot{x}^t &\equiv 0, \\ \mathrm{G}st &= gst, \\ \phi_r &= -2g_{\alpha\beta} \dot{x}^\alpha. \end{aligned}$$

Thus a particular solution of equation (I.) is

$$e^{\int \mathrm{G}_{\alpha\beta} \dot{x}^\alpha d\dot{x}^\beta} \mathrm{G}_{\alpha\beta} \dot{x}^\alpha \dot{x}^\beta = \text{const.} = \mathrm{A}, \quad . \quad . \quad . \quad \text{(II}'\text{.)}$$

the integral being taken along a path.

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* Richardson, 'Electron Theory,' p. 266.

(I.) may also be written in the form

$$\ddot{x}^i + \Gamma^i_{\alpha\beta}\dot{x}^\alpha\dot{x}^\beta = A\,e^{-\int G_{\alpha\beta}\dot{x}^\alpha dx^\beta}\cdot\dot{x}^i.$$

Let us next consider a change from the parameter s to t; our equation (I.) becomes

$$\left(\frac{dt}{ds}\right)^2\left[\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right]$$

$$= \left(\frac{dt}{ds}\right)^3 G_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\frac{dx^i}{ds} - \frac{d^2t}{ds^2}\frac{dx^i}{ds}.$$

If

$$\frac{d^2t}{ds^2}\Big/\left(\frac{dt}{ds}\right)^3 = G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}$$

or

$$\frac{dt}{ds} = e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{ds}dx^\beta},$$

then our equation can be written in the geodesic form,

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0. \quad . \quad . \quad . \quad . \quad \text{(III.)}$$

Equation (II′.) can then be written in the form

$$\frac{dt}{ds}G_{\alpha\beta}\dot{x}^\alpha\dot{x}^\beta = A,$$

or the solution of (III.) is

$$\left(\frac{dt}{ds}\right)^3 G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = A.$$

Now

$$e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\left(\frac{dt}{ds}\right)dx^\beta} = e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}\left(\frac{dt}{ds}\right)dt};$$

$$\therefore \quad e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}\left(\frac{dt}{ds}\right)dt}\cdot G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = A$$

is the form of the solution of (III.).

If $\quad G_{\alpha\beta} = m\,\bar{g}_{\alpha\beta}$,

m = invariant mass,

then $\quad M = m\dfrac{dt}{ds}$ = relative mass.

Thus we can write our solution in the form

$$e^{3\int M\bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta} \cdot \bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = \frac{A}{m}.$$

But since

$$e^{\int M\bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta} = e^{\Sigma\ \text{Action}},$$

we see that for any periodic path the Σ Action must be periodic; *i. e.*,

$$\int M g_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta = 2\pi n i, \qquad i = \sqrt{-1}, \quad n = \text{integer}.$$

Thus if we consider the most general motion of an electric charge without radiation of energy, we find that the motion is periodic only in case the following condition is satisfied:

$$\Sigma\ \text{Action} = nh,$$

where $n = \text{integer}$,

$h = \text{constant}$,

the action integrals being taken over a complete cycle.

The Quantum Conditions for periodic orbits are a particular case of this more general condition.

In conclusion, the writer wishes to express his gratitude to Professors E. P. Adams and L. Eisenhart for their interest and assistance during the writing of this paper.

NOTE (see page 915).—If we expand the potential ψ in Kirchhoff's solution in powers of $(t-r)$, we find that ψ is of the form,

$$\psi = \frac{1}{4\pi}\int\int\int\Big[f_1(x, y, z) + f_2(x, y, z)\ (t-r)^n + \text{terms in higher powers of } (t-r)\Big]\,dx, dy, dz,$$

where x, y, and z are independent of t,

for $(\rho u)' = (\rho u)_0 + (\rho u)_n(t-r)^n + \ldots\ldots$

$(\rho u)_i = \text{function of } x, y, z \text{ only},$

and $r' = \sqrt{(\xi-\alpha)^2+\beta^2+\gamma^2},$

where $\xi = A - a(t-r)^n$ from the equation of motion of the charge, and α, β, γ are the coordinates of the point where ψ is evaluated, where r=distance between position of electron at time t and point (α, β, γ).

Since $H=\text{rot } \psi$,

we find
$$\frac{\partial^m H}{\partial t^m}=\text{rot} \frac{\partial^m \psi}{\partial t^m}=0, \quad m<n,$$
for
$$r-t=0.$$

XCII. *A Possible Reconciliation of Bohr's Interpenetration Ideas with Sommerfeld's Relativistic Treatment of Electron Orbits.* By R. A. Millikan *and* I. S. Bowen *.

I. *Introduction.*

In a preceding article † we have presented a dilemma, each horn of which involves an inadmissible conclusion, and we have thus far suggested no way out of the difficulty.

The first purpose of this paper is to indicate the nature of the new assumption which it seems to us necessary to make in order to obtain some sort of a consistent scheme of interpretation, and the second purpose is to discuss the experimental data which lend some support to this assumption.

II. *Statement of the Dilemma.*

Our former work has shown that both the regular and the irregular doublet laws which had their origins in the study of X-rays are also valid throughout the whole field of optics. This fact leaves no alternative save to consider the s terms in optics as corresponding completely with the L_I M_I etc. terms in X-rays, the p_2 terms in optics with the L_{II} M_{II} terms in X-rays, and the p_1 terms in optics with the L_{III} M_{III} terms in X-rays. No escape from this conclusion, drawn in our former paper, seems to us to be possible.

In order to bring out sharply the nature of the difficulty which this last conclusion involves, we shall at first confine attention to orbits of total quantum number 2. The foregoing identification of optical and X-ray levels means definitely, as applied to these orbits, either (1) that we must adopt the choice made in optics and regard the L_{II} L_{III} orbits as both circles (2_2 orbits), such as the p_1 p_2 orbits are usually supposed to be in optics, or else (2) that we must adopt the choice heretofore made in X-rays and regard p_1 p_2 as two orbits of the shape 2_2 and 2_1, respectively, thus making the s and the p_2 orbits of the same shape, *i. e.* of shape 2_1.

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* Communicated by the Authors.

† Phys. Rev. xxiv. p. 223 (1924).

The objection to the first choice is that it makes L_I an ellipse of shape (2_1), and L_{II} a circle of shape 2_2, and then, in the case of the higher atomic numbers, the separation of these two energy-levels which is required by the application of the relativity principle (change of mass with speed) is about four times as great as the observed separation. Further, the screening constant of the circle should be greater than that of the ellipse, because of the greater penetration of the latter inside the screening electrons, so that the actual separation between the L_I and L_{II} levels should be larger than the relativity difference by the difference in the screening constants of the differently shaped orbits.

These considerations seemed so compelling that we said in the preceding article that there seemed to be no escape except to deny the applicability of the relativity principle *in toto* to electronic orbits. In view, however, of the complete quantitative success of this principle, especially in the interpretation of the behaviour of the spectra of atomic hydrogen and ionized helium, this denial seems well-nigh impossible.

The second choice, on the other hand, appears altogether impossible for a number of reasons, the most cogent among which is the fact, reported in our preceding paper, that we find that *the separation of the triplets as well as doublets for a series of atoms of like electronic structure but varying nuclear charge follows the relativity law.* Since the writing of the preceding paper many new triplets have been studied, and they completely bear out our former assertion as to the applicability of the relativity formula.

Since now in the second quantum state there are but two possible shapes of orbits (azimuthal quantum numbers) 2_1 and 2_2 to manipulate, it is absolutely necessary to call upon some *inner* quantum number—*i. e.*, some new orientation without change in shape—to account for at least one of the three energy levels here involved. *If, then, inner quantum numbers must be invoked anyway, it is in the interest of simplicity and consistency to invoke them throughout in explaining the behaviour of both triplets and doublets.* This argument seems to us an altogether conclusive one against the adoption of the change in azimuthal quantum number to account for the difference in the $p_1\ p_2$ energy levels.

III. *A Third Possibility.*

Since both of our suggested alternatives appear then impossible, our only escape is to find some break in the continuity of the proof of the exact applicability of the relativity formula to the atoms from uranium down to hydrogen.

To state our present conclusion in a word, we are herewith pointing out that it is just possible to make such a break between ionized helium and lithium, and thus save the relativity explanation for simple nucleus-electron systems like hydrogen and ionized helium, where, as a matter of fact, the evidence for the validity of the relativity formula is wonderfully exact.

In order to do this, however, we are forced to make a very difficult and strange assumption, viz.: that the remarkable fitting of all our data into the relativity formula for all the atoms from lithium up to chlorine, and then throughout the whole X-ray field, is accidental, and that there must be some other cause of a non-relativistic sort which is responsible for the behaviour of the spectra of all these elements, a cause which, though it has to do with changes in inner quantum numbers rather than azimuthal, yet leads not only to a fourth-power law, as does the relativity cause, but also to a formula having very closely the same numerical constants as has the relativity law.

To state the situation slightly differently, despite the fitting of the relativity law with the experimental data from lithium to uranium, we now throw overboard in all this field the relativity explanation of the observed doublet and triplet separations. We retain in both the field of optics and that of X-rays the optical selection principle, and make both $p_1\ p_2$ and $L_{II}\ L_{III}$ differ in inner quantum number, while the s and the p_2 levels, as well as the $L_I\ L_{II}$ levels, differ in azimuthal quantum number. At the same time we save the relativity explanation of the separation of the doublet of hydrogen and of ionized helium.

Landé * and others have before made this same choice to the extent of insisting that the selection principle used in optics be used also in the field of X-rays, but in so doing they have not been confronted with the new evidence contained in *our* observations of the great utility of the simple Sommerfeld relativity formula in leading to correct doublet and triplet separations, so that their choice was relatively easy. Nor have they attempted to show the difficulties of the position into which we are forced by such a choice. This we endeavour to do in the present paper.

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* *Zeit. f. Phys.* xvi. p. 391 (1923); xxiv. p. 88, and xxv. p. 46 (1924).

IV. *The New Success of the Relativity Formula.*

The two striking and altogether new successes of the relativity formula as shown in our work are:—

(1) The fairly close prediction which it makes of the screening due to the two K electrons in the spectra due to stripped atoms from lithium through nitrogen. This is presented in Table I. of the article in Phys. Rev. xxiv. p. 211. Also, since this paper was read before the American Physical Society in April 1924, Landé * has made and published a similar computation, using our preliminary and much less precise data published in January 1924 †.

(2) The extraordinarily accurate prediction of the variation of doublet separation with change in *total* quantum number. This is beautifully shown in Table I., *l. c.*, where we change the numerical constant of the relativity formula from ·365 to ·108 in carrying the computation of $\Delta\nu$ from the second to the third quantum state. A somewhat less perfect example of this success is seen in Tables II., V., VII., in all of which we found the computed and observed doublet separations varying with total quantum number about as the relativity formula demands. Landé also in Table IV. (*Zeits. f. Phys.* xxiv. p. 91) displays this sort of success.

By making the choice which we have made above, and treating the $2p_1$ $2p_2$ orbits as two circles differing only in orientation (inner quantum number), we are of necessity taking the position that these two successes of the relativity formula are purely accidental; and we are tacitly assuming that there is some entirely different cause of the separation of $2p_1$, $2p_2$, etc., which leads not only to the same type of variation of $\Delta\nu$ with both atomic number and with total quantum number as does the relativity cause, but which also leads to very nearly the same numerical constants as does the relativity cause. This is a difficult assumption to make, but there is absolutely no alternative to it if we wish to avoid both horns of the dilemma presented above. We are ourselves forced to make it, since neither of these horns appears to us admissible.

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* *Zeit. f. Phys.* xxiv. p. 32 (1924).

† Phys. Rev. xxiii. p. 33.

In making this assumption we are a little better off than we should have been in discarding the applicability of the principle of change in mass with speed altogether to electronic orbits, because we can now retain the relativity explanation of the behaviour of the hydrogen and helium spectra, where the evidence is most beautifully quantitative and where it is most difficult to conceive of any other cause.

V. *Our Assumptions and the Requirements which the New non-Relativistic Cause of Fine Structure must Meet.*

Having by this assumption separated hydrogen and helium from other atoms, it becomes our task to re-examine all of our data upon other substances in order to see how precisely our relativity formula does fit these data, and therefore how violent quantitative limitations we must impose upon our assumed new cause which is to lead to a formula closely resembling at least the relativity formula. Before making this analysis, we shall attempt to state briefly our present assumptions and our final conclusions as to the requirements which must be imposed upon this new cause.

When the system is a simple nucleus electron system, we assume that the fine structure of lines is wholly due to the relativity cause, so that we adopt as the fully adequate explanation of the character of hydrogen and ionized helium lines Sommerfeld's relativity equation :

$$\frac{\nu}{\mathrm{R}}=\frac{(\mathrm{Z}-\sigma)^2}{n^2}+\left[\frac{1}{4}+\frac{n-k}{k}\right]\frac{\alpha^2(\mathrm{Z}-s)^4}{n^4} \quad . \quad . \quad . \quad (1)$$

We adopt further, as applicable to all radiation, the selection principle used in optics, and therefore make $\mathrm{L_I}$, like $2s$, a 2_1 orbit. We also make $\mathrm{L_{II}}$ and $\mathrm{L_{III}}$, quite like p_2 and p_1, two circular orbits which differ only in orientation.

We assume that the orbits $\mathrm{L_I}$ and $\mathrm{L_{III}}$, like the orbits $2s$ and $2p_1$, are an ellipse (2_1) and a circle (2_2), respectively, the energies of which differ, first, because of the difference in the greater screening from the nucleus of the circular orbit than of the elliptical orbit, and, second, because of the relativity difference between these two orbits. This is equivalent to assuming that the $\mathrm{L_I}$ and $\mathrm{L_{III}}$ orbits differ in energy by the sum of the irregular doublet energy difference and the regular or relativity doublet energy difference. In optics the first difference is very large compared with the second, while in X-rays the second difference is much the larger.

With the aid of these assumptions we are able to retain the application of the relativity principle to all orbits. We now assume—and this is the point at which we try to escape from either of the two untenable horns of our dilemma—*that there is some cause acting by virtue of the difference in orientation of the two circular orbits* L_{II} *and* L_{III} *which increases the energy of the circular* L_{II} *orbit to about the amount which it would have had by virtue of relativity had it been a* 2_1 *orbit.* This cause may be magnetic in its origin, or electrostatic, or a combination of the two. The requirements imposed upon it are—

(1) that it must make the difference between L_{II} and L_{III} follow very nearly a fourth-power variation with atomic number, just as does the relativity cause ;

(2) that it must lead to nearly the same numerical constants as does the relativity equation ; and

(3) that it must make the doublet separation vary with total and azimuthal quantum numbers very closely as does the relativity equation (1).

The only advantage of this seemingly strange way out of our difficulty over that of discarding the applicability of the relativity principle altogether to electron orbits, is that we do not now demand that our new cause yield results which are so exactly in coincidence with those given by equation (1) as we should have to do if the new cause were required to fit the extraordinarily accurate data on hydrogen and ionized helium.

VI. *Imperfections in the Agreement between the Relativity Formula and Observed Doublet Separations.*

When we return now to the analysis of the doublet-separation data upon the atoms from lithium to uranium, we find, indeed, that they may be distinguished in a number of ways from the data available with a simple nucleus-electron system. Thus :

(1) They differ qualitatively in that all the elements from lithium to uranium have at least three two-quantum-number levels, viz. the $2s$, $2p_2$, $2p_1$ levels, or in X-rays the corresponding L_I, L_{II}, L_{III} levels, while in hydrogen and in helium, on the other hand, there are only the number of L levels required by the relativity theory—namely two.

This furnishes one justification for making a break in our interpretation between ionized helium and lithium.

(2) They differ quantitatively in that while equation (1) fits very exactly, according to the work of Paschen * and Shrum †, the observational data on simple nucleus-electron systems for which σ and s are both zero, it is impossible to make this assertion for any other systems. Indeed, in testing the relativity equation derived from (1) by subtracting two such equations corresponding to the two azimuthal quantum numbers 1 and 2, a process which yields

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{n^3k(k-1)}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which in this case $k=$ azimuthal quantum number 2, and $k-1=$ azimuthal quantum number 1, our procedure has always been simply to solve this equation for s, *which then becomes an arbitrary parameter.* For the whole series of stripped atoms, beginning with lithium, the value of s should, of course, have come out 2, since there are two screening electrons near the nucleus with all these atoms. It actually came out for stripped nitrogen 1·838, for carbon 1·858, for boron 1·884, for beryllium 1·937, and for lithium 2·019. None of these numbers is within the limit of experimental error of 2, and it will be seen that the fourth power makes a large error in $\Delta\nu$ appear as a small error in s.

We did, indeed, suggest in our preceding paper a logical explanation for the first four of these departures. Thus we assumed that the screening of the nucleus became less and less perfect as the orbit of the radiating electron came relatively closer and closer to the orbits of the screening electrons. Some such change in the perfectness of the screening with closer and closer approach to the screening electrons must take place in any case, so that the foregoing explanation must be regarded as qualitatively satisfactory. But the screening constant should then never exceed 2, no matter how far the radiating electron is removed. In the case of lithium, however, it does exceed 2 by 1 per cent., and a numerical computation shows that to cover this departure there should be an uncertainty of 7·4 per cent. in the separation of the lithium lines. Otherwise stated, their observed separation instead of being ·338 frequency units should have been ·365. The observations made by Kent ‡ on three different lines in which this doublet appears vary from ·336 to ·340, *i. e.* but one-sixth of the necessary difference. The relativity formula then, contrary to the less carefully considered opinion which we expressed in the preceding article, does not predict for this group of atoms the observed separation within what are probably *the limits of observational error.* Instead, the quantity s as we have used it is, within rather narrow limits, an arbitrary parameter with the aid of which we have forced the relativity formula into exact agreement with the observed facts.

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* *Ann. d. Phys.* l. p. 901 (1916).

† Proc. Roy. Soc. cv. p. 259 (1924).

‡ Astrophys. Journ. xl. p. 337 (1914).

The fourth-power variation with atomic number demanded by the relativity formula does, however, fit the observed doublet separations from lithium through nitrogen very closely. How closely may be seen from the fact that, if s is fixed at 2, the $\Delta\nu$ from lithium to nitrogen is proportional to $(Z-2)^{4\cdot13}$, thus showing that whatever the cause of the separation may be, it cannot follow anything resembling a third-power law of variation with effective nuclear charge as the Heisenberg theory * demands.

Also that the doublet separation varies with *total quantum number* almost exactly as the relativity formula demands is shown by the fact that the screening constant for the $3p$ doublet of C_{IV} was found in Table I. of the preceding article to come out with almost exactly the same value as the screening constant for the $2p$ doublet when we inserted the relativity constants ·365 and ·108, respectively, to compute these values of s.

When the same sort of careful analysis is made for the doublet separations found in the series of stripped atoms from Na to Cl, all seven of which we have now obtained, the screening constant s is again not predicted within the limits of experimental error, even in the limiting case of the most remote orbit upon which we can make observations. Here, again, the departure is in the same direction as in the case of lithium. Thus a glance at our former Table V. shows that the most remote orbit with which we have here worked is the circular $4f$ orbit in the case of Al_{III} and Si_{IV}. For the orbits much closer than this to the nucleus the table shows, quite as we should expect, that the screening constant comes out considerably less than the $(2+8)=10$ electrons in the two inner shells. This we explain qualitatively by the same considerations advanced for the behaviour of the lithium-to-nitrogen series—namely, imperfect screening for a too close approach to the screening electrons. In the case of the elliptical p orbits this too close approach may even be an interpenetration, and thus reduce s very considerably. In S_{VI} it is reduced from 10 down to as low a value as 5·57. But in the limiting case of the very remote circular orbit $4f$ the screening constant, as computed from the observed separations with the aid of the relativity formula, came out for Al_{III} 10·341 and for Si_{IV} 10·412. A careful numerical computation of the error in $\Delta\nu$ necessary to cover this difference from 10 makes it about 50 per cent., while the observed separations, namely ·38 for Al_{III} and 1·26 for Si_{IV}, ought to be correct to within 10 per cent. at most.

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* *Zeits. f. Phys.* viii. p. 273 (1922).

While, then, in the case of hydrogen and ionized helium the relativity formula predicts the fine structure quantitatively to as high a degree of precision as is attainable in the experimental work, in the case of both the lithium-to-nitrogen series and the sodium-to-chlorine series, even for remote orbits which ought to obey the laws of a simple nucleus-electron system, the relativity formula predicts results which depart from the observed data by somewhat more than the observational errors contained in those data. These facts justify to some degree, at least, making a break between helium and lithium and assigning different causes to the doublet separations in hydrogen and helium from those assigned in the case of the other atoms.

It is true that in the case of these atoms also, as in the case of the lithium-to-nitrogen series, the fourth-power variation with effective nuclear charge and the third-power variation with total quantum number (equation 2), both of which are consequences of the relativity theory, fit the observed facts, as shown in Table V. (*l. c.*), extraordinarily well. So that in throwing overboard relativity as a cause we are still obliged to find an equation of the same form as the relativity equation, a certain amount of latitude being allowed merely in the fixing of its numerical constants.

There is another bit of evidence that we have just brought to light which has some bearing upon this point. We have experimentally followed the doublet separations corresponding to $3d_2-3d_1$ and $4d_2-4d_1$ throughout the whole series of stripped atoms Mg_{II}, Al_{III}, Si_{IV}, P_V, and S_{VI}, and have found that these $\Delta\nu$'s do not progress at all in the way the relativity law demands. Nevertheless, at the end of the series, *i. e.* in S_{VI}, the separation appears to be rapidly approaching the relativity value *.

The real test of the relativity formula ought to be found in its ability to yield the correct screening constant in the *limiting* cases of very remote orbits where the system becomes essentially a nucleus-electron system, for any failure in the case of close-in orbits can be thrown back upon imperfect screening. Now the $3d$ and $4d$ orbits are, in fact, remote enough to make such large departures as have appeared in the diffuse series from $\mathrm{Mg}_{\mathrm{II}}$ to S_{VI} somewhat surprising and difficult to account for merely on the basis of imperfect screening. These departures, therefore, lend some support to the effort to differentiate sharply between the precise way in which hydrogen and helium follow the relativity formula and the rough way in which all other atoms behave with respect to it.

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* "The series Spectra of the Stripped Atoms of Phosphorus (P_V), Sulphur (S_{VI}), and Chlorine (Cl_{VII})," Phys. Rev. March 1924.

VII. *Consideration of Total Quantum Numbers Higher than Two*—M, N, *etc. Levels.*

For the sake of simplicity we have thus far confined our attention mainly to orbits of total quantum number two, *i. e.* to L orbits. From the point of view which we are here adopting, the five M levels shown in the figure, taken from Bohr and Coster*, would fit into our scheme as follows:—Levels M_{I} (3_1) and $\mathrm{M}_{\mathrm{III}}$ (3_2) differ in energy by a difference in screening constant due to difference in shape plus a relativity difference. M_{II} is then an orbit which is like $\mathrm{M}_{\mathrm{III}}$ in shape, but upon which our new hypothetical cause has operated so as to raise its energy to about the amount which it would have had by virtue of relativity had it been a 3_1 orbit. This brings the M_{II} line to essential parallelism with the M_{I} line. Similarly, $\mathrm{M}_{\mathrm{III}}$ and M_{V}, which correspond to the differently shaped 3_2 and 3_3 orbits, respectively, also differ by a screening constant plus a relativity difference, while M_{IV} has been raised by the assumed new cause to such a point as to produce essential parallelism between the M_{IV} and $\mathrm{M}_{\mathrm{III}}$ lines.

The fact that our postulated new cause must produce very nearly the same effect as a relativity cause, both as regards the difference between the energies of 3_1 3_2 orbits and 3_2 3_3 orbits imposes another limitation upon this cause which is almost as severe as those imposed by the necessity of varying both with effective nuclear charge and with total quantum number precisely as the relativity theory demands. In other words, the postulated cause is required to demand the same *variation* (1) with effective nuclear charge, (2) with total quantum number, and (3) with azimuthal quantum number as is demanded by the relativity principle. But in view of the undetermined parameter s which is used in making the relativity formula fit the facts in the case of all optical and X-ray spectra except those of hydrogen and

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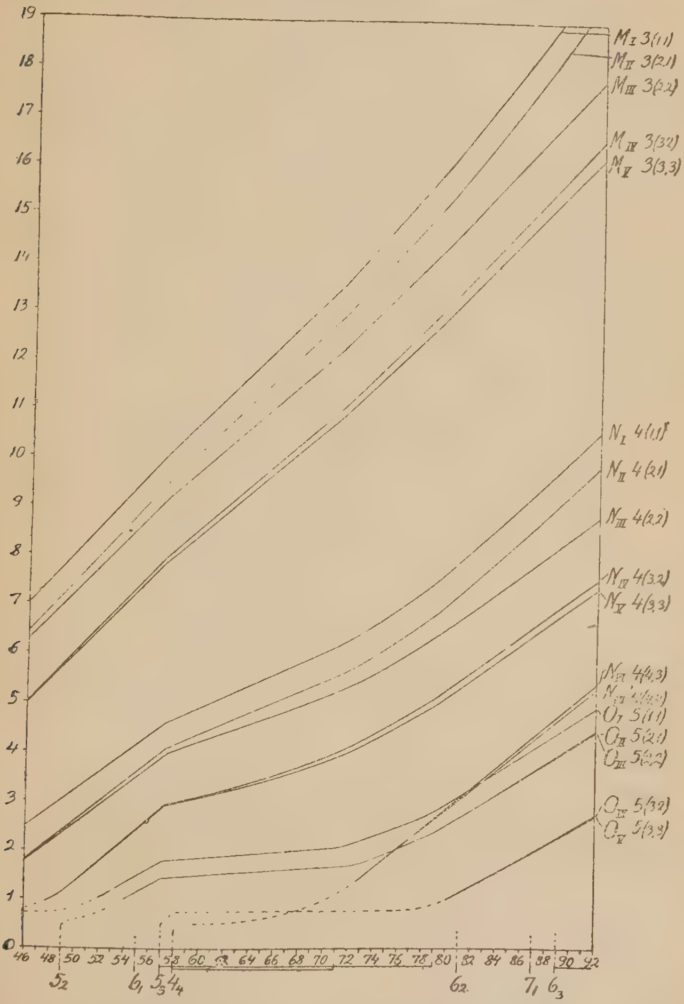
* *Zeit. f. Phys.* xii. p. 369 (1923).



ionized helium, it cannot be said that we impose anything like so exacting a quantitative condition upon our new cause as we should if we denied the relativity cause *in toto*, and hence made the new cause also take care of the spectral behaviour of hydrogen and ionized helium.

VIII. *The Bearing of the Paschen-Back Effect.*

A crucial test of the foregoing hypothesis that there is a difference in kind between the fine structure of the lines produced by a simple nucleus-electron system like atomic hydrogen and ionized helium—a structure which we have assumed to have a *real* relativity cause—and the fine structure found in the spectrum of lithium and atoms of higher atomic number—a structure which we have assumed to be due to changes in inner rather than azimuthal quantum number—should be found in a comparison of the behaviour of these different types of fine structure in magnetic fields.

Thus each of the components of the hydrogen and helium doublets ought in such a field to show the *normal* Zeeman effect, while the effect of a magnetic field upon the doublets in lithium and the like ought to be of an entirely different nature. *As a matter of fact, in weak magnetic fields this difference is known to exist in a very striking way*, the lithium doublet and the like showing the so-called anomalous Zeeman effect, while the normal Zeeman effect is shown by each of the lines of the doublet of hydrogen and ionized helium. So far as it goes, this fact lends strong support to our hypothesis.

When the magnetic fields are strong, however, it is well known that Paschen and Back * discovered that the fine structure in lithium disappears entirely, and that there is found but a single line having a normal Zeeman effect, *as is to be expected if the difference between the components of the lithium line is due to a magnetic cause*; for a sufficiently strong external field might then be expected to overcome entirely the weak magnetic influence which produces the doublet.

Upon our present theory we should not expect the Paschen-Back effect to be observable in hydrogen and ionized helium at all. In strong magnetic fields, however, so far as experimenting has now gone, the evidence seems to favour the conclusion that the Paschen-Back effect is found in hydrogen †. This weakens somewhat the force of our argument for the difference in kind between the hydrogen and lithium doublets, though the respective normal and anomalous Zeeman effects which these substances show in weak magnetic fields still makes them in one particular, at least, *distinctly* different. Further work is needed to show with certainty whether in strong fields the Paschen-Back effect is actually exhibited by hydrogen and ionized helium or not.

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* *Ann. der Physik*, xxxix. p. 897 (1912) and xl. p. 900 (1913).

† Oldenburg, *Ann. der Physik*, lxvii. p. 253 (1922). Försterling & Hausen, *Zeit. f. Phys.* xviii. p. 26 (1923).

IX. *Recapitulation.*

The evidence for a difference in kind between the fine structure of the lines of the two lightest elements, atomic hydrogen and ionized helium, and that of lithium and all the elements beyond it is so good, despite their apparent similarity in behaviour in strong magnetic fields, that we propose to attribute the doublets of atomic hydrogen and ionized helium to a true relativity cause, and to introduce a new non-relativistic cause, which, however, obeys an equation almost exactly like the relativity equation, to account for the behaviour of lithium and the elements of higher atomic number. This is the only possible way to retain both Bohr's interpenetration ideas and Sommerfeld's relativistic treatment of electron orbits; and both of them seem at present to demand retention. To find a new cause for the relativity-doublet-formula with only a little leeway in the value of the numerical constants is a problem worthy of the efforts of the theoretical physicist.

Norman Bridge Laboratory of Physics.
California Institute of Technology,
Pasadena, California.
November 24, 1924.

XCIII. *An Experimental Investigation of the Dynamical Equation of the Process of Gas-Sorption.* *By* D. H. BANGHAM, *M.A.*, *and* W. SEVER, *M.Sc. of Manchester University*[*].

THE problems presented by the phenomena of absorption (or, more generally, "sorption") and occlusion remain largely unsolved at the present time, in spite of the numerous theories which have been put forward to account for them. The theory of Langmuir[†] that the "sorbate" forms at the interface between two phases a film one (and in exceptional cases two and three) molecules in thickness has been eminently successful in cases where the molecules concerned consist of long chains of atoms; and it has been satisfactorily applied to certain types of gas-solid equilibria at very high temperatures. It does not, however, account for the well-marked phenomena of occlusion, and its application to account for all the changes taking place when a finely-divided solid is exposed to a gas is therefore conditional on the inability of the solid to occlude (*i.e.* dissolve) the gas. The essential differences between the two types of phenomena have been emphasized by McBain [*].

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[*] Communicated by Mr. D. L. Chapman, M.A., F.R.S.

[†] Langmuir, Journ. Amer. Chem. Soc. xxxviii. p. 2221 (1916); xl. p. 1361 (1918).

It has recently been shown experimentally [†] that a surface of glass, when freshly exposed to such gases as ammonia, carbon dioxide, sulphur dioxide, and nitrous oxide (at approximately constant pressure) takes up gas in accordance with the equation

$$\log s = \frac{1}{m} \log t + \text{constant},$$

where s is the quantity of gas sorbed or fixed at time t reckoned from the moment of first exposure.

This equation has been found by the authors and their collaborators to be valid in a large number of instances. It agrees well, for example, with the data given by McBain [‡] for the sorption of iodine by charcoal from solutions in benzene and toluene, and with certain of the data of Bergter [§] for the sorption of air by the same solid. It has been confirmed in these laboratories by Mr. J. B. M. Herbert for the system carborundum-ammonia gas, and by Mr. J. Stafford for the system graphite-oxygen (under low pressures). A similar type of equation has been found to govern the reverse process of desorption (in its early stages), and fair agreement with many of Richardson's [‖] data for the decay of the positive ionization from hot wires obtained by applying it in the differential form.

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[*] McBain, Trans. Faraday Soc. xiv. p. 202 (1919).

[†] Bangham and Burt, Proc. Roy. Soc. A. cv. p. 481 (1924).

Loc. cit.

[§] Bergter, *Ann. der Physik* (iv.) xxxvii. p. 472 (1912).

[‖] The saturation current at a given time corresponds in the notation used here to $-ds/dt$. In one case Richardson's data allow the integrated form of the equation to be tested directly. Richardson (Phil. Mag. viii. p. 405 (1904) remarks:—

"The positive leak appears always to decay asymptotically with the time, although it does not follow an exponential law. . . . . Another way of demonstrating the same thing is to measure the total quantity Q of electricity received by the electrometer at various times. Since dQ/dt is equal to the current we have, if the simple (that is, the exponential) formula holds,

$$dQ/dt = Ae^{-kt}, \quad \text{whence} \quad Q = Q_0(1-e^{-kt}),$$

if Q_0 is the charge received by the electrometer after an infinite time has elapsed. In seeking to verify this formula curves such as those shown . . . . were obtained. It was impossible to fit these curves by so

The equation has met with no explanation, either in terms of Langmuir's theory or otherwise. The systems instanced, however, are all characterized by extreme reluctance to attain equilibrium (according to the equation none should ever be reached) and this fact, taken in conjunction with the observations that the amounts of gas taken up far exceed those necessary to form monomolecular films, points to the conclusion that the gas molecules are capable of penetrating the solid.

The present investigation is an attempt to follow the sorption process beyond the range of its obedience to the equation given above; it was thought that if it proved possible to examine the mode of approach of the sorption-value to its limit, valuable information would be obtained as to the mechanism of the change.

Carbon dioxide was chosen as the experimental gas, and a quantity of fine glass-wool, tightly packed into a tube and then carefully cleaned and dried, was used as sorbent. Before each experiment the glass was subjected to a drastic process of vacuum-heating, the containing tube being in connexion with a bulb cooled in liquid air to condense out the gases as fast as they were disengaged from the solid.

Judging from previous results with such a system, equilibrium between the carbon dioxide and glass might well have taken an impracticably long time to achieve; advantage was, however, taken of a particular tube which showed a behaviour somewhat different from the others examined *.

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simple a formula as the above; the theoretical curves become much flatter after a few minutes have elapsed, when the two coincide near the origin."

The experimental values of Q as read from the published graphs for

t=0·57, 1·32, 2·09, 3·38, 5·1, 8, 11, 18, 24, and 28 minutes,

are, respectively,

28, 35, 40, 48, 54, 60, 65, 70, 75·5, and 77 units.

The applicability to these results of a time-equation of the type considered in this paper is indicated by the approximate constancy of the quotient $Q/t^{\frac{1}{4\cdot 0}}$, which takes the respective values: 32, 33, 33, 35, 36, 36, 36, 34, 34, 32. It should be emphasized (*vide* Richardson, Proc. Roy. Soc. A lxxxix. p. 507 (1914)) that the positive carriers in such a case were not charged molecules of occluded gases, but *the ions of potassium (and sodium)*.

* The tube actually used was one of a batch prepared for the earlier experiments already described (Proc. Roy. Soc. A. cv. p. 481 (1924), and it was filled, cleaned, and dried in exactly the same way and at the same time as the others. The single difference lay in the fact that it had been filled with carbon tetrachloride (to calibrate its deadspace) before

The results obtained with this tube confirmed the conclusion that in its initial stages the sorption is governed by the characteristic equation given above, but the constant m, instead of taking the anticipated value of ca. 12, was some two to three times smaller. Thus a far larger range of sorption values became accessible to measurement within a reasonable time, and, further, there was every hope of finding a deviation from the equation for large values of t.

The System of Measurement.

Since it was hoped to record results at short intervals over long periods of time, a somewhat elaborate apparatus was constructed, which will not be described in detail. It was of the greatest importance to keep the pressure of the carbon dioxide constant with a minimum of control on the part of the operator; and since this virtually necessitated (among other things) the immersion of the whole system in a constant temperature bath, the optical method of determining pressures was discarded, and a method was used whereby the falling of the pressure below a standard value was indicated by the making of an electrical contact. To maintain the pressure while sorption was in process, the effective volume of the system was periodically decreased by admitting mercury through an electrically controlled valve into a large glass bulb which functioned as the gas reservoir.

At the beginning of each experiment the reservoir was filled with gas to a pressure slightly lower than that at which the standard-pressure gauge had been arranged to function. Mercury was next admitted through the valve until the breaking of the electric contact indicated that the standard pressure had been reached. The pressure itself was read off a simple manometer in the gas-train, which was then cut off from the gas-reservoir by closing a tap. A volume of mercury rather greater than the deadspace volume of the sorption bulb was next admitted through the valve, and a tap connecting the gas-reservoir to the sorption bulb opened. As soon as the pressure fell to the initial value (as indicated by the making of the contact) more mercury was admitted

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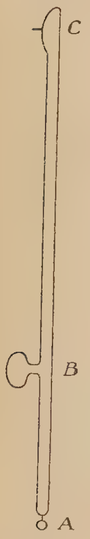
the final vacuum-heating. Carbon tetrachloride was chosen as the calibrating liquid since the use of water might have been detrimental, and it was anticipated that the non-polar nature of the tetrachloride would render it comparatively easy to remove. Apart from the different behaviour of the glass towards carbon dioxide, there was nothing to indicate that the drastic process of vacuum-heating to which the tube was subjected had not succeeded in removing the calibrating liquid completely.

to replace the gas lost by sorption. In cases where too much mercury had been admitted the excess could be run out through a tap. After the first few minutes of each experiment it was found possible, with all-night attention, to keep the pressure constant within very narrow limits indeed. Except for a short capillary tube carrying the tap between the sorption-bulb and the gas-reservoir, the entire system including the gauge was packed with ice. The quantity of mercury added up to any given time was determined by weighing periodically the bottle from which it had been taken.

The gauge consisted primarily of a mercury-filled U-tube of sufficiently wide bore to obviate significant capillary effects. Floating on the mercury in its barometer limb was a small glass bulb rigidly attached to a hinged lever-arm. This lever-arm is shown diagrammatically in the sketch (fig. 1), A being the hinge (made of platinum sealed into the glass wall of the barometer-head), and B being the float. At C a platinum wire was sealed into the lever-arm which made or broke contact with a pool of mercury contained in a bulb blown into the containing barometer-head. The barometer head itself, which was expanded to enclose the lever-arm, was connected by quill tubing to a phosphorus pentoxide tube and mercury pump, so that any gas that developed could be removed without difficulty. Since throughout each experiment the quantity of mercury in the U-tube remained fixed and its temperature constant at 0° C., the level of the mercury served to determine completely the pressure within the apparatus.

Fig. 1.



It is well known that the mercury-contact method of determining the heights of mercury columns is usually unsatisfactory though the cause of this is not fully understood. It was hoped in the present instance that the use of the lever principle (whereby errors were reduced in the ratio of AB to AC) and the fact that the contacts were maintained in a vacuum, would lead to more satisfactory results. These hopes were to some extent justified. As long as the apparatus was in constant use the indication of the standard pressure was clear and definite, and concordant results could be obtained with little trouble. When, however, in the later stages of the experiments the apparatus had been left idle for considerable periods, it was frequently very difficult afterwards to obtain concordance. In the earlier experiments an attempt was made to make the admission of mercury into the gas-reservoir automatic by causing the closing of the barometer-head circuit to operate the relay controlling the valve for admission of mercury. This method, although it had the advantage of keeping the contacts working in the absence of the operator, had finally to be given up on account of vibrational disturbances caused by traffic in the vicinity. The effect of these was to operate the valve and admit mercury long after the pressure inside the apparatus had been raised above the standard value.

Discussion of Results.

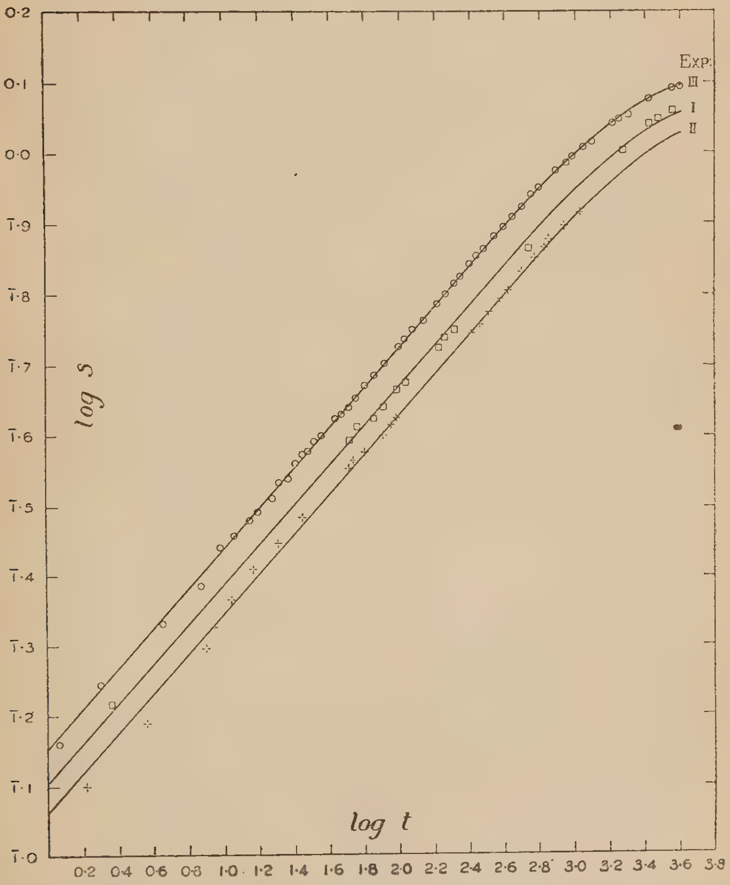
It has already been stated that the results confirm the validity of the "power" expression for the initial stages of the sorption process. This is illustrated in fig. 2 where the logs of s and t are plotted against each other. The graphs refer to three consecutive experiments all carried out at a pressure of 12·5 mm. Their linear portions cover a 5- or 6-fold range of sorption values, and it will be noticed that the lines are closely parallel.

Many of the experiments had to be discontinued on account of the erratic behaviour of the contacts following long periods of idleness. In certain cases, however, they were continued for some weeks, strictly isothermal conditions being adhered to throughout. The data for one of these protracted experiments (carried out at a pressure of 147·5 mm.) appear in the table below; in this experiment consistent data were obtained even in the later stages, as the table will show.

Apart from the extreme probability that glass is capable of dissolving small quantities of carbon dioxide, the authors have recently obtained evidence that the "power" time-law is obeyed in cases where the penetration of the solid phase by the gas can hardly be questioned. The chief interest of the present results lies, therefore, in their comparison with those to be expected on the basis of the theory of diffusion. Assuming the penetration of the solid to take place in this instance, there is every reason for concluding that "adsorption" or surface-sorption accounts for a negligible proportion only of the total effect; for the time-equation itself clearly constitutes an argument against the partition of s into two terms. In this respect the behaviour of glass as a sorbent stands in marked contrast to that of sodium chloride, for Mr. Herbert, using the latter substance, has obtained time-sorption curves which suggest that the s-value is, in their case, sharply divided into two terms, of which one only is a function of the time.

While the simplicity and general applicability of the time-sorption equation are in themselves strong arguments in favour of the view that the sorption-process is one subject to its own peculiar laws, it is nevertheless somewhat difficult to prove that the validity of such an equation in the early stages of the process necessarily involves a complete departure from the normal laws of diffusion and heat-conduction. The rate-of-sorption data obtained in the final stages of the process, on the other hand, should provide strong evidence either for or against such a departure. In discussing the question we shall merely assume that, the pressure being constant, the gas molecules at the interface are replaced from

Fig. 2.



the gas phase as fast as they diffuse into the interior of the glass.

The normal laws of diffusion would require that in the very early stages of the process (before the size and shape of the solid impose any serious limitation to the total number of gas-molecules taken up) the rate of sorption should vary as $t^{-\frac{1}{2}}$. The complete expression for the rate is given, however, by the sum of a series of exponential terms, which we may write

$$A_1 . e^{-b_1 Dt} + A_2 . e^{-b_2 Dt} + A_3 . e^{-b_3 Dt} \ldots\ldots$$

In this expression D is the unknown diffusion constant (supposed independent of the concentration), and the coefficients $b_1, b_2, b_3, \ldots.$, which form a *divergent* series, are conditioned by the size and shape of the solid. Since for small values of t the sum of these terms must vary as $t^{-\frac{1}{2}}$, it is clear that in the early stages the series of exponentials converges only very slowly, and is therefore unsatisfactory as a test of agreement. For very large values of t, however, the convergence should be extremely rapid, and as s approaches closely to its limit the rate of change should be governed by the first exponential term only.

An examination of the data renders it very doubtful whether this last generalization can apply to the sorption process under consideration, the latter part of the rate-of-sorption curve being difficult to represent in terms of exponentials in t. If, on the other hand, $t^{1/m}$ is taken as the argument ($1/m$ being the constant value of $\frac{d \log s}{d \log t}$ in the early stages), it is found that a single exponential term in $t^{1/m}$ gives very fair agreement with the experimental results. Since the evaluation of the index $1/m$ from the straight portions of the $\log s/\log t$ graphs takes no cognisance of the appearance of a sorption limit, a still better agreement is obtained with a slightly higher value of this index *. In the following table experimental values of s at the times shown are compared with those calculated from the equation

$$\log_{10} \frac{3{\cdot}07}{3{\cdot}07 - s} = 0{\cdot}0501 t^{0{\cdot}364}.$$

In this equation 3·07 c.c. (N.T.P.) is the limiting value of s for $t = \infty$. This quantity of carbon dioxide, concentrated as a dense film at the external surface of the glass fibres, would have formed a layer of about three molecules' thickness. n their experiments with glass fibres and carbon dioxide at

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* It is clear, from the type of equation considered, that the evaluation of this index from the $\log s/\log t$ graphs is unsatisfactory.

TABLE I.

Experimental pressure = 147·5 mms.

Time	c.c. at N.T.P.		Diff.	Time	c.c. at N.T.P.		Diff.
(mins.).	*s* obs.	*s* calc.	1=0·01c.c.	(mins.).	*s* obs.	*s* calc.	1=0·01c.c.
4·50	0·55	0·55	—	336	1·88	1·90	—2
6·08	0·65	0·62	+3	379	1·94	1·95	−1
7·50	0·67	0·66	+1	436	2·00	2·00	—
10·1	0·75	0·73	+2	474	2·03	2·03	—
13·0	0·80	0·78	+2	514	2·06	2·07	−1
16·8	0·86	0·85	+1	549	2·10	2·10	—
20·3	0·88	0·90	−2	579	2·13	2·12	+1
24·2	0·95	0·95	—	619	2·15	2·14	+1
28·6	0·97	1·00	−3	794	2·27	2·24	+3
39·7	1·10	1·10	—	1,115	2·41	2·38	+3
48·3	1·12	1·16	−4	1,400	2·49	2·46	+3
53·3	1·20	1·20	—	2,340	2·62	2·63	−1
65·9	1·26	1·26	—	2,554	2·64	2·66	−2
70·1	1·29	1·29	—	3,980	2·78	2·78	—
73·8	1·30	1·31	−1	5,560	2·84	2·86	−2
98·0	1·41	1·41	—	6,640	2·85	2·89	−4
132	1·51	1·52	−1	10,000	2·96	2·95	+1
164	1·59	1·60	−1	12,730	2·97	2·99	−2
187	1·66	1·66	—	16,700	3·01	3·01	—
209	1·71	1·70	+1	19,630	3·02	3·02	—
*242	1·76	1·76	—	22,540	3·04	3·03	+1
266	1·79	1·80	−1	26,900	3·04	3·04	—
279	1·82	1·82	—	37,150	3·10	3·05	+5
300	1·85	1·84	+1	46,550	3·05	3·06	−1
318	1·87	1·87	—				

* At this stage a minute quantity of mercury was spilt; its amount was, however, so small that it could be estimated (by eye) almost to within the normal experimental error.

about the same pressures, Evans and George † found the sorption to correspond to a a layer of 5·5 molecular diameters. The difference is undoubtedly due to differences in the quality and treatment of the glass, and in particular to the presence in the solid (as part of its structure) of different amounts of water in the two cases. Considered by themselves these sorption values do not represent an overwhelming excess over those required by Langmuir's theory, especially if a furrowed surface be ascribed to the fibres of glass. Far greater sorption values have, however, been recorded for other gases ‡, and have been found to be controlled by laws similar to those here considered §.

Interesting comparisons can be drawn between the results recorded here and those of the older experiments of Bangham and Burt, since the same glass was used in the two cases, and it was submitted to the same vacuum-heat treatment. The fact that the course of the sorption was so different in the two cases is by no means inconsistent with the view that the same equilibrium value might ultimately have been reached at the same pressure. If this assumption be made calculation shows that after 48 hours' exposure to carbon dioxide at 147 mms. pressure * the glass of Bangham and Burt was less than 50 per cent. saturated, in spite of the fact that their early sorption values were considerably greater than those recorded in the table. Moreover, even supposing the equation $s=kt^{1/12}$ (which was found to govern the process during the first 48 hours) to have continued valid throughout, the equilibrium value would have been closely approached only after 2–3 years.

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† Evans and George, Proc. Roy. Soc. A. ciii. p. 190 (1923).

‡ Evans and George, *loc cit.*

§ Bangham and Burt, *loc. cit.*

Summary and Conclusions.

1. The equation $d \log s/d \log t = \text{constant}\left(\frac{1}{m}\right)$ for the early stages of the process of sorption on glass surfaces is confirmed, the experiments showing it to be valid over a range of sorption values of ca. 6 : 1. The value of $1/m$ is shown to be highly susceptible to changes in the past history of the glass, and probably to the presence of minute amounts of impurity.

2. Time-sorption data beyond the range of obedience to the above equation have been obtained, and are shown to be closely represented by a formula of the type

$$\log \frac{\sigma}{\sigma - s} = kt^{1/m},$$

where σ is the limiting value of s as t approaches infinity.

This approximates to the former equation for small values of s and t.

3. Equations of this type appear to be applicable in a large number of dynamical processes involving the passage of matter from the gaseous to the solid state, and *vice versa*. While there are reasons for believing that the phenomena occurring are not restricted to the boundary layer, but involve a transport of matter through the solid medium, strong evidence is given that the laws governing the changes concerned are not those of ordinary diffusion.

The authors' thanks are due to Dr. Burt and Mr. Angus Core for their continued interest in this work, and for their many helpful suggestions.

We acknowledge also the receipt of a grant from the Brunner Mond Research Fund, which has materially assisted in defraying the expenses of the investigation.

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Manchester University.

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* No actual experiment was carried out at this pressure, but the data recorded are sufficiently full to allow the interpolation to be made without difficulty.

XCIV. *The Crystal Structure of Magnesium Fluoride. By* H. E. Buckley, *M.Sc., Assistant Lecturer in Crystallography, and* W. S. Vernon, *M.Sc., Assistant Lecturer in Physics, Manchester University*[*].

Introductory.

MAGNESIUM fluoride (MgF_2) is found in nature as the mineral selläite. It is described by Groth[†] as crystallizing in the dipyramidal class of the tetragonal system with $a : c = 1 : 0{\cdot}6596$. The chemically prepared magnesium fluoride is a finely-divided powder consisting of minute crystals which belong to the same class of symmetry as the natural mineral.

Determinations of the density by different authorities show rather large discrepancies. E. G. Cossa gives 2·857, Struver 2·972, and Sella 3·153. The value found by the authors as the result of X-ray measurement (3·11) lies between the two latter measurements.

Experimental.

The powder method of crystal analysis was used in this investigation. A cylindrical camera was used of 2·5 cm. radius, designed on the lines of the camera described by Bradley[‡]. The source of X-rays was a Siegbahn tube with a copper anticathode.

With a tube current of 20 milliamperes, satisfactory results were obtained with an exposure of one hour. The magnesium fluoride used was the purified chemical precipitate, and this was mounted on a hair with fish-glue.

The first film which was taken in this manner was found to have on it lines which were very broad and diffused, indicating that the particular powder was sub-microscopically fine. It was heated to redness for several hours in order to enable the minute particles to coalesce, and the mass was then uniformly ground up in an agate mortar. This treatment was found to be successful, all the lines on subsequent films appearing sharp and bright. An additional photograph was also taken, using the apparatus described by Bradley (*loc. cit.*), the result of this exposure being used to corroborate the results obtained by us. The films were measured by means of a travelling-stage microscope, and the results, averaged out for eight films, are included in the first column of Table I.

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[*] Communicated by Prof. W. L. Bragg, F.R.S.

[†] Groth, *Chemische Krystallographie*, i. p. 205.

[‡] Bradley, A. J., "Arsenic," Phil. Mag. xlvii. p. 657 (1923).

TABLE I., with Copper ($K\alpha$) Radiation.

Average Distance in mm. from centre.	Angle of Reflexion.	Spacings in Å.U. Obs.	Spacings in Å.U. Calc.	*h k l.*	Obs. order of Intensity.	Calc. order of Intensity.
—	—	—	4·654	100	—	—
11·95	13° 27′	3·311	3·300	110	4	4
—	—	—	3·076	001	—	—
15·45	17 26	2·568	2·567	011	26	28
—	—	—	2·327	200	—	28
17·70	19 56	2·257	2·249	111	2	2
19·28	21 43	2·080	2·085	210	5	6
—	—	—	1·858	201	—	—
23·50	26 28	1·727	1·727	211	2	2
24·82	27 58	1·644	1·650	220	8	10
—	—	—	1·551	300	—	—
26·64	30 0½	1·539	1·538	002	9	10
28·10	31 38½	1·469	1·472	310	28	28
—	—	—	1·461	102	—	—
28·45	32 4Z	1·450	1·450	221	19	19
29·97	33 47½	1·389	1·396	301	1	1
			1·392	112		
31·47	35 27½	1·329	1·329	311	19	20
32·75	36 54	1·283	1·288	320	24	24
			1·283	022		
34·38	38 44	1·230	1·235	212	10	10
35·80	40 20⅓	1·192	1·192	321	26	28
36·83	41 28	1·162	1·164	400	22	23
38·42	43 17	1·123	1·127	410	5	5
			1·124	222		
39·64	44 39	1·095	1·099	330	13	13
—	—	—	1·092	302	—	—
—	—	—	1·088	401	—	—
41·30	46 30	1·061	1·060	411	13	16
—	—	—	1·051	132	—	—
42·40	47 45	1·040	1·042	420	17	21
—	—	—	1·035	331	—	—
—	—	—	1·029	003	—	—
44·80	50 28	0·998	1·001	103	28	28
45·63	51 24	0·985	0·988	421	15	13
			0·988	322		
46·23	52 4	0·976	0·978	113	24	16
—	—	—	0·939	303	—	—
49·91	56 14	0·929	0·931	500	19	22
			0·931	430		
			0·924	402		
50·67	57 4	0·917	0·920	123	15	15
51·34	57 50	0·909	0·912	412	10	8
			0·909	510		
			0·892	332		
53·06	59 45	0·891	0·891	431	7	6
			0·891	051		
—	—	—	0·875	511	28	24
—	—	—	0·874	223	—	27
56·37	63 30	0·860	0·860	520	18	18
			0·863	422		
57·51	64 46	0·854	0·855	033	10	9
58·65	66 5	0·842	0·842	133	22	24

Σ (53 planes) $= 41$

The Unit Cell.

The spacings corresponding to these lines are found in the third column of Table I.

Using the density = 3·11 estimated above, and with *two molecules* of MgF_2 to the unit cell, a series of spacings may be calculated which show a close correspondence (column 4, Table I.) with the observed values.

The dimensions of a unit cell containing two molecules of MgF_2 are as follows :—

"a" =	4·654 Å (calc.) ;	4·660 Å (obs.).
"c" =	3·076 ,, ;	3·078 ,,
$a:c$ =	1 : 0·6596 ,, ;	1 : 0·660 ,,

In the fifth column of Table I. are found the (indices of the) planes associated with each line on the film. In the sixth column the lines are grouped according to their observed intensities. Thus the strongest line is labelled 1, the remainder go in descending order of magnitude to 28, and those planes of which the intensities lie below the "28" value are not sufficiently strong to be observed or do not give any reflexion at all.

Position of the Atoms in the Structure.

A study of the lines given in Table I. shows that with lines of the type $(0kl)$, where $(k+l)$ is odd, the spacings are halved. This is characteristic of two space-groups, viz. D_{4h}^{14} and C_{4v}^{4}. In both cases, since there are only two magnesium atoms, the latter must be situated on a centred tetragonal prism whose coordinates are (000) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. There are four fluorine atoms, and these in D_{4h}^{14} are placed at points with coordinates

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ 0;\ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ 0;\ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{1}{2};\ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{1}{2}\quad \ldots \quad (A)$$

or

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ \tfrac{1}{4};\ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ \tfrac{1}{4};\ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{3}{4};\ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{3}{4},\quad \ldots \quad (B)$$

where "p" may assume positive or negative values. In C_{4v}^{4} the four fluorine atoms are to be found at points whose coordinates are

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ q;\ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ q;\ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ 0-q;\ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ 0-q,$$

where again "p" may assume positive or negative values. In D_{4h}^{14} (001) and (003) should be absent, while in C_{4v}^{4} these lines should be present. Neither is to be found on the films. It would also appear, from the occurrence of a strong (002) line, that the two sorts of atoms lie in the same plane, in which case the arrangement C_{4v}^{4} will assume the higher symmetry of D_{4h}^{14}. The latter arrangement therefore appears more than likely. Finally it will be shown that for a particular value of "p," in D_{4h}^{14} marshalling, there is a good agreement between calculated and observed intensities.

In D_{4h}^{14} the F atoms may be in the same plane as the Mg atoms, or they may interlace these. A choice between these two possible types is therefore necessary, and recourse must be made to a comparison of calculated and observed orders of intensity for the different lines. In order to evaluate the intensities of reflexion given by planes with different arrangements of atoms, certain assumptions as to the relative scattering power of magnesium and fluorine atoms are necessary. The rate of falling off of intensity with increase in the glancing angle must also be considered. The latter is assumed to be proportional to the inverse square of the sine of the angle, and, as a fair approximation, the relative scattering power of Mg and F was taken as 10 : 10, *i.e.* the two kinds of atoms are practically of equal weight. As a preliminary test, the two possible arrangements in which $p=0$, viz. $\frac{3}{4}, \frac{3}{4}, 0$; $\frac{1}{4}, \frac{3}{4}, 0$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{2}$ and $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$, were tried. Neither of these gives satisfactory orders of intensities for the lines. In both cases all calculated intensities are found to be identical with each other except those for lines of the type $(2h.2k.2)$, *e.g.* 002, 022, 222, 042, 242, and for the latter lines the arrangement in which Mg and F atoms are in one plane gives fair results when compared with the observed orders of intensity for these lines, while the alternative, in which Mg atoms are interleaved with F atoms, gives totally incorrect orders. This is confirmed by the previous observation regarding the strength of the (002) line. There appears, therefore, little doubt that the Mg and F atoms do lie in one plane, and that the arrangement marked "A" of D_{4h}^{14} is the correct one. There is a displacement "p" *to* or *from* a Mg atom parallel to the (110) plane with coordinates, if displaced in the latter direction, of

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ 0;\ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ 0;\ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{1}{2};\ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{1}{2}.$$

If the displacement be *towards* an Mg atom, "p" will then have an opposite sign to that given. There will then be an extraordinarily high value for the (110) spectrum, whereas the latter was not observed to be as strong as (112+301) or (111) or (211) spectra. Moreover, it will give a very small value for the distance Mg–F. The displacement is therefore most likely in a direction *away* from an Mg atom.

Calculations were made of intensities, on this arrangement, of the following lines:—110, 011, 200, 111, 210, 211, 112+301, 220, 222+410, 400, 330, 033, 332+051+431 (eighteen in all). Values of the parameter were taken for every five degrees from 100° to 130°. The resulting intensities were arranged in descending order of magnitude and compared with the observed order for these lines. The differences in order for each line were noted, and a sum (Σ) of these for each value of "p" taken, as shown in Table II.

Table II. (18 planes).

$p \times 360° =$	130°	125°	120°	115°	110°	105°	100°
$\Sigma =$	30	30	23	19	19	24	31

There is a minimum error in the neighbourhood of 110°–115°. This region was explored more thoroughly, every possible plane from (100) to (133), fifty three in all, being used. The results are given in Table III.

Table III. (53 planes).

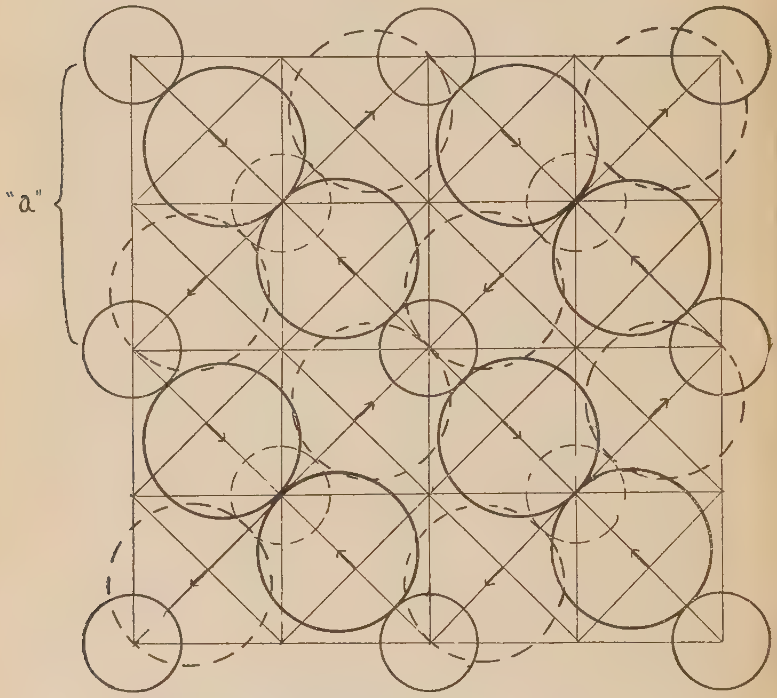
$p \times 360 =$	115°	114°	113°	112°	111°	110°
$\Sigma =$	53	52	41	53	61	72

The best value of "p," therefore, is in the region of $\frac{113}{360}$, where the average error per line is about $\frac{3}{4}$ of 1 unit. The complete order of calculated intensities for this value of "p" is given in the last column of Table I.

Description of Structures.

Magnesium fluoride crystallizes on an arrangement possessing the symmetry of space-group D_{4h}^{14}. "Mg" atoms are located on a centred-tetragonal space-lattice with a unit interval of "a"=4·650 Å and "c"=3·078 Å, while the "F" atoms lie in the same 001 planes as their "Mg" neighbours and are associated with them, grouped in pairs about each (fig. 1). The distance apart of Mg to F is 2·07 Å. This is in substantial agreement with the value obtained by adding Bragg's later radii for these elements, viz. 2·08 Å. It is interesting to note that the structure is similar in type to rutile (TiO_2), in spite of the apparent chemical differences in both atoms and valencies involved. That this similarity is not merely fortuitous is shown by a glance at Table IV., where a comparison of the crystallographic properties of rutile, MgF_2, and cassiterite is given. The agreement is very striking for substances so apparently dissimilar.

Fig. 1.



Larger circles denote fluorine atoms, smaller circles magnesium atoms.

TABLE IV.

	Rutile.	MgF_2	Cassiterite.
$a:c$.	1 : 0·644	1 : 0·660	1 : 0·672
Cleavage.	100 & 110 good.	100 & 110 good.	100 & 110 good.
Mol. per unit cell.	2	2	2
Dimensions of unit cell $a =$	4·58 Å.	4·66 Å.	4·67 Å.
Dimensions of unit cell $c =$	2·92 ,,	3·08 ,,	3·14 ,,
Distance RR′.	TiO = 1·99 Å.	MgF = 2·07 Å.	SnO = 2·08 Å

The constants of MgF_2 appear to be intermediate in character between those of rutile and cassiterite.

Summary.

Magnesium fluoride (MgF_2) is found to crystallize on a structure possessing the symmetry of D_{4h}^{14}. The unit cell is a tetragonal prism with $a=4{\cdot}660$ Å, $c=3{\cdot}078$ Å, and $a:c=1:0{\cdot}660$. The distance of closest approach of Mg to F is 2·07 Å, agreeing with a calculated value of 2·08 Å. The structure is similar to that of rutile (TiO_2), with which it possesses several properties in common.

The authors desire to take this opportunity of expressing their gratitude to Professor W. L. Bragg for his help and advice, also to Mr. R. W. James and Dr. A. J. Bradley for assistance rendered during the course of the research.

XCV. *The Arc Spectra of Silver and Copper.*

By A. G. SHENSTONE, Ph.D.*

[Plate IX.]

THE spectrum obtained from the ordinary copper or silver arc in air contains a great many spark lines often imperfectly distinguishable from the true arc lines. As a first step in the disentangling of the series relationships of these metals, experiments have been carried out to separate completely the lines due to the ionized and unionized atoms. A preliminary report appeared in 'Nature' of October 4, 1924 (vol. cxiv. p. 501).

If a sufficiently high density of metal vapour can be supplied, arcs can be maintained in these metals at voltages as low as six volts. Even under these conditions, however, it cannot be known with certainty that all spark lines have been eliminated owing to the presence of cumulative ionization. But if the vapour is bombarded with low velocity electrons and no arc is allowed to form, there should be emission of lines due to the unionized atom only. This can be accomplished by means of the three electrode arrangement devised by Foote, Meggers, and Mohler †, in which the electrons from a hot filament are accelerated through a grid into a force free space. The apparatus used for silver is shown in fig. 1.

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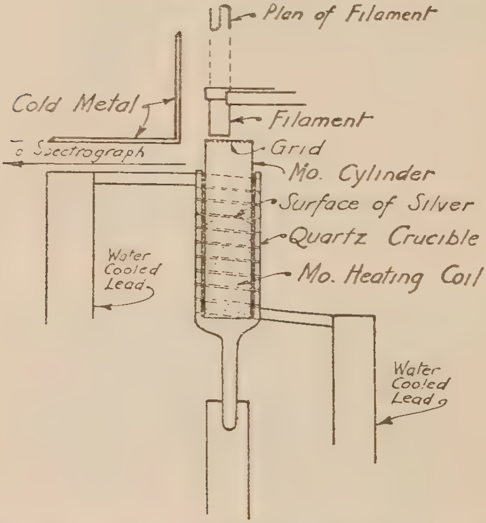
* Communicated by the Author.

† Phil. Mag. xlii. p. 1002–15 (1921).

The 15 mil tungsten filament was placed very close to the grid at the top of the crucible, and the electrons were accelerated by a suitable potential, usually about 10 volts, applied between the filament and the grid. The radiation resulting from the bombardment of the silver atoms in the mouth of the crucible was photographed by means of a small quartz spectrograph. The apparatus was enclosed in a water-cooled, vacuum-tight metal container, provided with quartz windows, and the rate at which the windows silvered over was reduced by a flow of hydrogen at about ·01 mm. pressure.

Fig. 1.



Under such conditions a maximum exposure of about three-quarters of an hour could be made.

Using either copper or silver, it is not difficult with this apparatus to obtain the "single-line" spectrum by applying a sufficiently low voltage. To obtain the complete arc spectrum of silver a potential of nine to ten volts was employed. In agreement with the analysis of the silver spectrum as given by Fowler [*], only one pair of lines (λ 2061·19 and λ 2069·85) was obtained below the first pair of the principal series (λ 3280 66 and λ 3382·86). The former pair was measured as accurately as possible on plates given by a perfectly adjusted small Hilger quartz spectrograph, and they were found to agree much more closely with the calculated values than with the measurements of Piña *. There is little doubt from these experiments that the accepted energy levels of the silver atom are correct.

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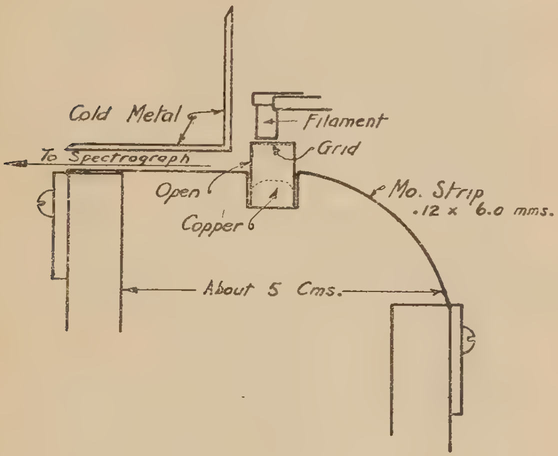
[*] Fowler, "Report on Series in Line Spectra," p. 111 (1922).

For the equivalent experiment with copper another form of furnace was found more suitable (fig. 2).

Fig. 2.



The crucible in this case was a cylinder of molybdenum strip having an opening toward the window of the apparatus and a grid at the top. A heating current of 70 amperes, through the supporting molybdenum strip, produced copper vapour at a sufficient rate for the experiment. As in the work with silver, a 15 mil filament was used, giving, at 10 volts, an emission of about 6 to 10 m.a.

The lines † of the copper spectrum photographed under these conditions are given below, together with additional lines (marked with an asterisk) which appear in the arc at about 8 volts and ½ amp. The intensities are estimated roughly from the best plate obtained of the low-voltage arc spectrum. The spectrum was obtained on a Schumann plate (Table I.).

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* Fowler, "Report on Series in Line Spectra," p. 111 (1922).

† Wave-lengths in this paper, except where noted, were obtained from Kayser und Konen, *Handbuch der Spectroscopie*, vii. pp. 334–352.

TABLE I.

	Intensities.	
	Hasbach.	8 Volt.
2024·33 *		1
† 2138·44 *	1*u*	1
2165·06	1*u*	4
2169·49 *	2*u*	0
2171·75 *	1*u*	0
2178·91	1*u*	4
2181·68	1*u*	4
2199·65 *	6R	2
2214·56 *	6R	3
2215·65 *	4R	2
2225·665	2R	3
2227·74 *	6R	2
2230·071	6R	3
2236·22 *	1*u*	0
2238·43 *	2*u*	1
2244·240 *	2	1
2260·493 *	4	0
2263·09 *	6R	1
2293·832 *	8R	3
2392·629 *	8*r*	1
2441·625	6	2
2492·142	8	3
2618·381	10*r*	5
2766·388	8	4
2824·375	8	4
2882·937	4	4
2961·177	6	5
2997·363 *	4	1
2998·384 *	2	
3010·840	5	2
3036·105	6	5
3063·416	6	5
3073·803 *	4	1
3093·993 *	6	2
3156·623 *	3	0
3194·103 *	6	1
3208·236 *	4	1
3247·550	10R	20
3273·967	10R	20

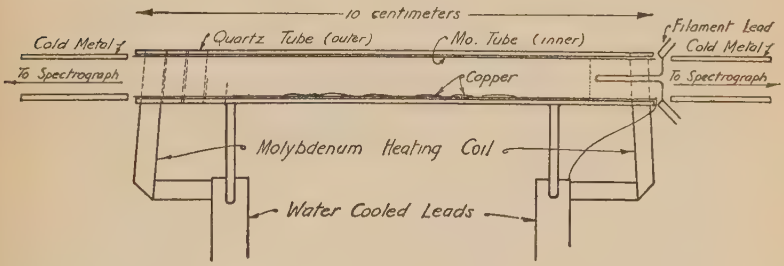
(It will be noted that this list includes λ 2178·91, which was given incorrectly in my letter to 'Nature' as λ 2179·39).

† Simeon and Dreblow ('Nature,' cxiv. p. 751, 1924) give 2138·49.

The wave-length given for the line λ 2024·33 is the value obtained from combinations. This line was measured carefully on five plates of the ordinary arc, using a perfectly focussed small spectrograph, and the following values were obtained :—2024·30, ·35, ·30, ·36, giving an average of 2024·33. The value given by Piña is λ 2024·05. The line is quite strong in the low voltage arc and certainly has no accompanying arc-line of comparable intensity in the neighbourhood.

If the scheme of the copper arc spectrum is as given by Fowler, all lines in the region below λ 3148, the limit of the subordinate series, should be produced by transitions to the levels 1*s*, X, or levels of the same nature of X. Observations of absorption would differentiate between these alternatives. An apparatus (fig. 3) was therefore set up to determine which of these many lines were absorbed by copper vapour.

Fig. 3.



The apparatus consisted of a molybdenum tube within a quartz tube heated by means of a molybdenum coil. Near one end was a grid and in that end an arc was struck from a hot filament to the inner tube. The whole apparatus was enclosed as before. Simultaneous photographs of the spectrum were taken by two small quartz spectrographs placed opposite the two ends of the tube. A comparison of the two spectra shows that the following lines were definitely absorbed by the column of copper vapour :—

λ 2165·06
2225·665
2244·240
2441·625
2492·142.

The two lines λ 2181·68 and λ 2024·33 were not quite certainly absorbed, and the line λ 2178·91 was not sufficiently resolved from 2179·37. But all of these are certainly $1s-p$ lines, as will be seen from combinations. By a slightly different method the absorption of λ 3247·550 and λ 3273·967 was shown [*].

The level called X by Dunz is known from Zeeman data to be an md_2 level [†]. Dr. Ruark, of the Bureau of Standards, Washington, suggested the value of the other level of this pair md_1 as 51105, which has been altered to 51105·5 to fit the combinations which have been calculated. Using this value for md_1, $md_2=49062{\cdot}6$ and $1s=62308$, the combinations given in Table II. are found.

In a footnote to his paper "Linienspektren und Atombau" (*Ann. d. Phys.* lxxi. s. 268, 1923) Bohr mentions that Werner has found the term md_1 and a number of combinations with it. No values are given.

In Table II. the wave-lengths and intensities are, where possible, Hasbach's. In the region of long wave-lengths the measurements of Meggers and Aretz have been used.

It will be seen from Table II. that the two pairs of levels np_a and np_b, np_c and np_d have abnormally large separations 829·7 and 371·6. They are also reversed from the usual order, *i. e.*, the larger term has the inner quantum number 2. If these two pairs are successive members of a series of p levels, it is strange that there are not present in the spectrum any lines resulting from the lower members of the same series. Moreover, the relative intensities of the combination lines are not at all regular. Ruark, Foote, and Mohler have found inverted doublet terms in helium, but in that case the intensities of the p_d lines were such as would be expected from the inner quantum numbers [‡].

Of the pair of levels np_e and np_f, the smaller, np_f, has the inner quantum number 2, and they may, therefore, be the normal $3p_2$ and $3p_1$. This conclusion is given weight by the fact that one plate has been obtained on which the only lines appearing below the principal pair are λ 2181 and λ 2179, although usually in the low voltage arc this is not the strongest pair. Moreover, it is seen that the intensities of these two lines are relatively much greater in the low voltage arc than in the ordinary arc in air. The remaining two levels, np_g and np_h, are very difficult to fit into a doublet system. np_h combines strongly with md_1 and md_2 and has, therefore, inner quantum number 2. The line $1s—np$ at λ 2024·33 is apparently the only arc line in a large region of the spectrum. No evidence is available as to the fineness

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[*] W. Grotrian, *Zeits. f. Physik*, xviii. 3–4, pp. 169–182 (1923).

[†] Paschen-Goetze, 'Seriengesetze der Linienspektren,' foot of p. 68.

[‡] Ruark, Foote, and Mohler, Opt. Soc. Am. Journ. vol. viii. p. 17, Jan. 1924.

Table II.

	ν (calc.).	λ.	ν (obs.).
	$2p_2=31772·8$.	$2p_1=31524·4$.	
$1s—2p_2$	30535·2	3273·97 (10R)	30535·2
$md_2—2p_2$	17289·8	5782·16 (8)	17289·8
$1s—2p_1$	30783·6	3247·55 (10R)	30783·6
$md_1—2p_1$	19581·1	5105·55 (8*u*)	19581·1
$md_2—2p_1$	17538·2	5700·25 (6)	17538·2
	$np_a=22194·0$.	$np_b=21364·3$.	
$1s—np_a$	40114·0	2492·142 (8)	40114·0
$md_1—np_a$	28911·5	3457·856 (3)	28911·4
$md_2—np_a$	26868·6	3720·770 (2)	26868·6
$1s—np_b$	40943·7	2441·625 (6)	40943·9
$md_2—np_b$	27698·3	3609·300 (2)	27698·3
	$np_c=17763·9$.	$np_d=17392·3$.	
$1s—np_c$	44544·1	2244·240 (2)	44544·7
$md_1—np_c$	33341·6	2998·384 (2)	33341·6
$md_2—np_c$	31298·7	3194·103 (6)	31298·7
$1s—np_d$	44915·7	2225·665 (2R)	44916·4
$md_2—np_d$	31670·3	3156·623 (3)	31670·3
	$np_e=16487·2$.	$np_f=16428·8$.	
$1s—np_e$	45820·8	2181·68 (1*u*)	45821·7
$md_2—np_e$	32575·4	3068·912 (2)	32575·4
$1s—np_f$	45879·2	2178·91 (1*u*)	45880·2
$md_1—np_f$	34676·7	2882·937 (4)	34676·7
$md_2—np_f$	32633·8	3063·416 (6)	32633·8
	$np_g=16135·2$.	$np_h=12925·0$.	
$1s—np_g$	46172·8	2165·06 (1*u*)	46173·6
$md_1—np_g$	34970·3	2858·737 (2)	34970·2
$md_2—np_g$	32927·4	3036·105 (6)	32927·4
$1s—np_h$	49383·0	2024·33 (?)	49383·0
$md_1—np_h$	38180·5	2618·381	38180·2
$md_2—np_h$	36137·6	2766·388 (8)	36137·6

of this line. The level np_g combines strongly with md_2. In the ordinary arc it also combines with md_1, giving λ 2858·74, but no line at this point is obtained in the low-voltage arc, indicating that this level may have inner quantum number 1. The line $1s$—np_g λ 2165·06 is a very fine line in the spark spectrum under high dispersion and can hardly be double. In the arc spectrum it shows a single fine reversal.

In the following table are found calculated energy levels which may be further *p*-terms:—

TABLE III.

	ν (calc.).	λ.	ν (obs.).
Q=7280·3.			
md_1—Q	43825·2	2281·07 (2)*	43825·4
md_2—Q	41782·3	2392·629 (8*r*)	41782·3
$1s$—Q	55027·7	1817·3 (1)	55026·7
M=5964·3.			
md_1—M	45141·2	2214·56 (6R)	45141·6
md_2—M	43098·3	2319·561 (4)	43098·3
$1s$—M	56343·7	1774·4 (2)	56357·1
$2s$—M	13206·8	7570·09 (5)	13206·3
K=4888·9.			
md_2—K	44173·7	2263·09 (6R)	44173·7
$1s$—K	57419·1	1741·6 (5)	57418·5
$2s$—K	14282·2	7000·02 (1*u*)	14281·7
J=4358·4.			
md_1—J	46747·1	2138·49 (1*u*) †	46747·1
md_2—J	44704·2	2236·22 (1*u*)	44704·3
$1s$—J	57949·6	1725·9 (3)	57940·8
$2s$—J	14812·7	6749·29 (2*u*)	14812·3
N=4188·2.			
md_1—N	46917·3	2130·700 (1)	46918·0
md_2—N	44874·4	2227·74 (6R)	44874·4
$2s$—N	14982 9	6672·23 (3)	14983·4
R=3943·2.			
md_1—R	47162·3	2119·80 (0)*	47159·4
md_2—R	45119·4	2215·65 (4R)	45119·4
$2s$—R	15227·9	6565·54 (3*u*)	15226·8

* Wave-lengths due to Piña.

† Simeon and Dreblow (*loc. cit.*).

Of these, M and J may possibly be $5p$ and $6p$, but in that case no line occurs corresponding to $1s$—$4p$.

Further possible levels are given in the following table :—

TABLE IV.

	ν (calc.).	λ.	ν (obs.).
	A = 18581·9.		
md_1—A	32523·6	3073·803 (4)	32523·6
md_2—A	30480·7	3279·823 (3)	30480·7
	B = 17901·8.		
md_1—B	33203·7	3010·840 (5)	33203·7
md_2—B	31160·8	3208·236 (4)	31160·8
	E = 15709·8.		
md_1—E	35395·7	2824·375 (8)	35395·7
md_2—E	33352·8	2997·363 (4)	33353·0
$2p_2$—E	16063·0	6223·66 (3*u*)	16063·3
	F = 7523·8.		
md_1—F	43581·7	2293·832 (8R)	43581·7
md_2—F	41538·8	2406·661 (6)	41538·7

The lack of further combinations with these terms makes their interpretation very doubtful at present. It may be that here, and also in some cases in Table III., we are dealing with p' and d' terms : in particular A and B are probably d' terms, although the intensities are not such as would be expected. Zeeman types of some of the important lines should settle such points.

In an attempt to find confirming combination lines, the differences of all the terms, old and new, of the copper spectrum have been taken, with very little result. The following may have some significance :—

TABLE V.

	ν (calc.).	λ.	ν (obs.).
np'_a—3*s*	12734·5	7848·55 (1)	12737·7
np_a—V	16537·7	6045·09 (2*u*)	16537·8
np_a—$4d_1$	15276·9	6544·51 (1*u*)	15275·7
np_a—$4d_2$	15273·2		
np_b—$4d_1$	14447·2	6920·09 (4*u*)	14446·7
np_c—4*s*	12127·2	8242·27 (1)	12129·3
np_e—J	12128·8		
$2p_1$—np_f	15095·6	6621·61 (4)	15097·9
np_f—R	12485·6	8006·27 (2)	12486·7
$2p_1$—Q	24244·1	4123·27 (2*u*)	24245·8
$2p_2$—E	16063·0	6223·66 (3*u*)	16063·3

The whole arc spectrum from the infra red to λ 3100 has been examined for frequency differences corresponding to the various pairs of terms found in this research. A few were found, but were probably fortuitous. It is, perhaps, important that one of Rydberg's constant frequency differences 680·1 equals the difference between the terms A and B; but there are no terms derivable from this relation which give any further combinations. In all, the difference 680·1 occurs 9 times, 680·0 3 times, 680·2 once. The remainder of Rydberg's doublets are accurately repeated sufficiently often to be considered real, but they have no apparent connexion with the terms calculated in this paper.

Of the lines found experimentally as arc lines in this research, there remain without interpretation:—

λ 2169·49
2171·75
2199·65
2230·071
2238·43
2260·493
2961·177
3093·993

Of these, λ 2169 and λ 2171 seem to form a pair. Considered as due to combinations with md_2, these lines would yield terms 3031·4 and 2983·3. The line λ 1687·2 corresponds sufficiently closely with $1s$—3031·4. If the very strong line λ 2961·177 is due to a transition to md_2, the term 15302·1 may be a companion to E=15709·8, and they might then be an inverted pair of p' terms.

The line given as λ 2199·65 by Hasbach is in reality a double line. A plate, which Professor McLennan has kindly allowed me to use, taken on a Hilger E1 spectrograph, shows, without any doubt, two reversals in this line at λ 2199·57 and λ 2199·73. From the former of these two lines the following combinations may be calculated, using a term V=5656·3:—

	ν (calc.).	λ.		ν (obs.).
md_1—V	45449·2	2199·57	(6R)	45449·2
md_2—V	43406·3	2303·109	(6)	43406·2
$1s$—V	56651·7	1765·5	(3)	56641·2

The wave-number difference between the two components of λ 2199 is 3·2.

The lines usually assigned to combinations with the

f terms in the copper spectrum are very unsatisfactory. In particular the line λ 2369·88, given as md_2—4f, does not appear at all in the low-voltage arc though it is a strong line in the arc. It is probably a spark line. The line λ 2260·49, which Dr. Ruark suggested as md_1– 4f, appears faintly in the low voltage arc. The wave-number separation of these two lines is only 2041·0 instead of 2042·9. The lines λ 4056·7 and λ 4015·8, supposed to be 2p_1—4f and 2p_2—4f, have a separation of 250·9 instead of 248·4, but in this case the error may be due to the broadness of the lines.

The lines λ 3598·01 (2u) and λ 3566·14 (1u) with a wave-number separation of 248·2 are suggested as 2p_1—5s and 2p_2—5s. In that case 5s=3739·1.

It is realized that the present investigation of the copper spectrum is not only incomplete but unsatisfactory in that it does not decide the nature of many of the terms found. It is hoped, however, to rectify this by further investigations. The large number of arc lines still unexplained, among them many of great intensity, makes it evident that we are dealing with a spectrum of considerable complexity. It would not be surprising if quartet terms entered into the structure.

Summary.

1. Experiments are described on the ultra-violet spectra of low-voltage arcs in silver and in copper vapour. A table of the lines obtained is given.

2. The line absorption of copper vapour has been found experimentally. Ten lines in the ultra-violet are absorbed. The various combinations calculated from these data are tabulated. No series is evident in these lines.

3. Further terms are calculated from the low-voltage arc lines, using a term md_1=51105·5.

Description of Plate.

1. Spectrum of copper arc at 15 volts and 1·2 amperes. This shows some spark lines. The 8-volt plate referred to above has become too scratched for reproduction.

2. Simultaneous photographs of the copper spectrum showing absorption. The arc was at 25 volts and ·5 ampere. On the reproduction, the absorption of the marked lines only is visible.

3. Double reversal in λ 2199·65.

It was impossible to carry out all of the experimental work alone, and I am very grateful to Mr. C. Barnes and others in the laboratory who, on various occasions, kindly assisted me. I am very much indebted to Professor McLennan, who has always given me his interested advice and assistance and who has placed at my disposal all the facilities of the laboratory.

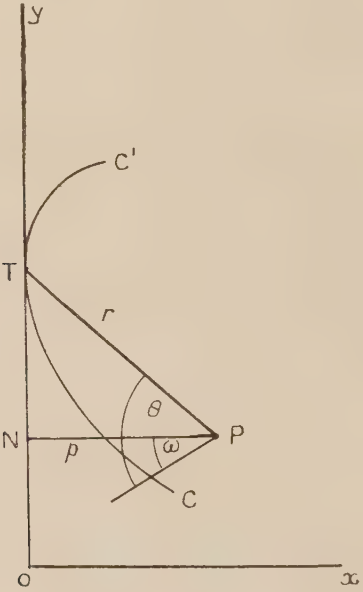
Physics Laboratory,
University of Toronto,
Jan. 13, 1925.

XCVI. *On the Use of Roulettes for Graphical Integration.*

By ALFRED A. ROBB, *Sc.D., F.R.S.*[*]

LET CC′ be a curve and P a point fixed with respect to it.

Let the tangent at any point T of the curve be taken and let the perpendicular from P to it meet the tangent in the point N.



Let the tangent roll without slipping on the curve, turning in the clockwise direction in the figure.

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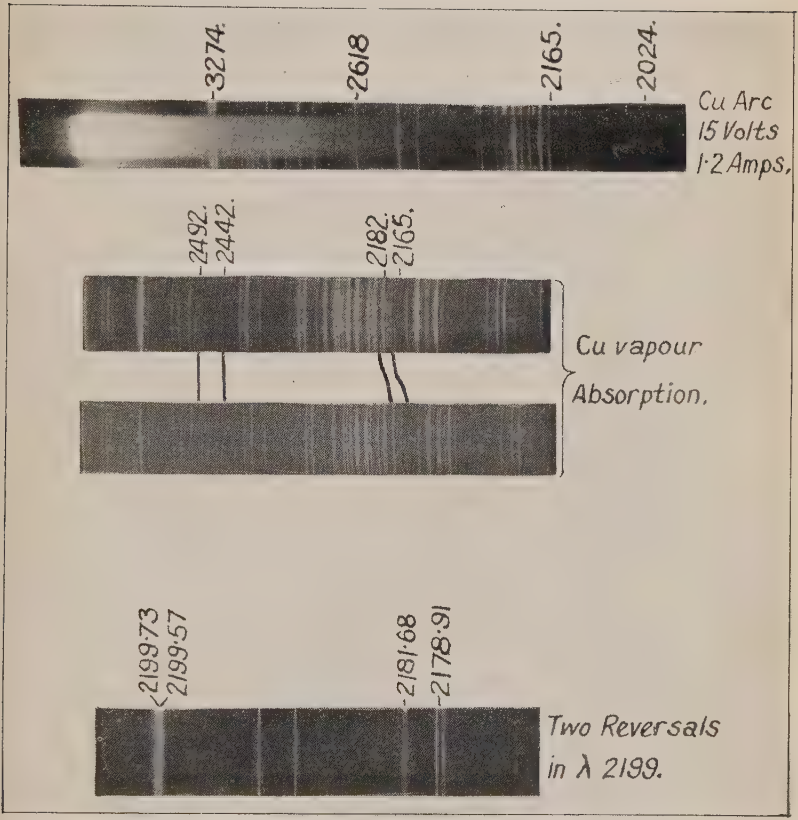
[*] Communicated by the Author.


3274.
2618
2165.
2024.
Cu Arc
15 Volts
1·2 Amps.
2492.
2442.
2182.
2165.
Cu vapour
Absorption.
2199·73
2199·57
2181·68
2178·91
Two Reversals
in λ 2199.

Let the perpendicular length PN be denoted by p and the angle turned through by p from some fixed direction be denoted by ω.

Let ds be the length of an element of arc of the curve corresponding to an increase $d\omega$ of ω.

Then it is a well-known result that

$$\frac{d^2p}{d\omega^2}+p = \frac{ds}{d\omega},$$

and it is also well known that the length $\mathrm{NT}=\frac{dp}{d\omega}$.

The same formulæ will obviously hold if we suppose the tangent to remain fixed while the curve rolls along it without slipping, but turning in the opposite or anti-clockwise direction in the figure.

Now let us suppose the tangent to be taken as the axis of y of a set of rectangular cartesian coordinates and that the curve rolls along it.

Then, if x and y be taken as the coordinates of P with respect to this set of axes, we have

$$p = x$$

and $$\mathrm{ON} = y.$$

But $$\mathrm{ON} = \mathrm{OT}-\mathrm{NT}$$

$$= \mathrm{OT}-\frac{dp}{d\omega},$$

while $$\mathrm{OT} = s+\text{constant}.$$

Thus $$s-\frac{dp}{d\omega}+\text{constant} = y.$$

Suppose now that the p and ω equations of the curve be expressed in the form

$$\int\frac{f(p)}{p}\,dp+\mathrm{K} = \omega,$$

where $f(p)$ is an arbitrary function of p.

Then

$$f(p)\frac{dp}{d\omega} = p,$$

and so

$$\left(\frac{d^2p}{d\omega^2}+p\right)-\frac{d^2p}{d\omega^2}-f(p)\frac{dp}{d\omega} = 0$$

or

$$\frac{ds}{d\omega}-\frac{d^2p}{d\omega^2}-f(p)\frac{dp}{d\omega} = 0.$$

Integrating, we get

$$s - \frac{dp}{d\omega} - \int f(p)\,dp = \text{constant}.$$

Thus substituting for p and $s - \frac{dp}{d\omega}$, we get

$$y = \int f(x)\,dx + \text{constant}.$$

If then we can express $\int \frac{f(x)}{x}\,dx$ in terms of known functions, but cannot so express $\int f(x)\,dx$, (a thing which very frequently happens), we can pass from the rolling curve expressed in p and ω coordinates to the relation between y and x for the roulette described by P and so obtain a graphic integration of $\int f(x)\,dx$.

In tracing the rolling curve, the position of the point T is obtained from the relation

$$\text{NT} = \frac{dp}{d\omega},$$

which, when we express $\frac{dp}{d\omega}$ in terms of p, becomes

$$\text{NT} = \frac{p}{f(p)}.$$

If r be the length of the radius vector PT and θ be the angle made by r with the direction (fixed with respect to the rolling curve) from which ω is measured, then

$$\tan(\theta - \omega) = \frac{\text{NT}}{\text{PN}} = \frac{1}{f(p)}.$$

But

$$\int \frac{f(p)}{p}\,dp + \text{K} = \omega,$$

and so we get

$$\left.\begin{aligned} \theta &= \int \frac{f(p)}{p}\,dp + \tan^{-1}\left(\frac{1}{f(p)}\right) + \text{K}, \\ r &= p \sec\left\{\tan^{-1}\left(\frac{1}{f(p)}\right)\right\}. \end{aligned}\right\}$$

Since the elimination of p between these equations is not generally practicable analytically, it is better to retain p as an auxiliary variable, by means of which we may calculate corresponding values of θ and r and so trace out the rolling curve.

It will be observed that the possibility of doing this depends upon the possibility of expressing $\int \frac{f(p)}{p}\,dp$ in terms of known functions; but we shall show later how we may make use of this result in constructing a general method of graphic integration.

The equation giving r in terms of p may also be written in the (in some respects) simpler form:

$$r = \sqrt{p^2 + \left(\frac{p}{f(p)}\right)^2};$$

but, in addition to the ambiguity of sign introduced by the square root, this is not really so convenient for purposes of calculation, since the former expression may readily be evaluated by means of trigonometrical tables.

As a simple example of the direct application of the above, suppose that we wish to evaluate the logarithmic integral:

$$\int \frac{dx}{\log x},$$

which, as is well known, cannot be expressed by elementary functions.

Put

$$f(p) = \frac{1}{\log p}.$$

Then

$$\begin{aligned}\int \frac{f(p)}{p}\,dp &= \int \frac{dp}{p\log p}\\ &= \log(\log p) + \mathrm{K}.\end{aligned}$$

Thus

$$\left.\begin{aligned}\theta &= \log(\log p) + \tan^{-1}(\log p) + \mathrm{K},\\ r &= p\sec\{\tan^{-1}(\log p)\}.\end{aligned}\right\}$$

If this curve be traced in polar coordinates and be rolled along the axis of y, then its pole will trace out the curve

$$y = \int \frac{dx}{\log x} + \text{constant}.$$

In practice the rolling curve might be traced on a sufficiently large scale on a stiff piece of cardboard and then cut out carefully.

It might then be caused to roll along a straight edge (preferably faced with rubber to prevent slipping) and fixed so as to coincide with the axis of y on a piece of squared paper. The point of a pencil might then be passed through a small hole in the cardboard at the pole P, and thus the curve

$$y=\int f(x)\,dx$$

might be traced out directly.

If the portion of the rolling curve with which we are dealing is convex to P instead of being concave, as in the figure, then the point P will be situated in a part of the cardboard which will be cut away.

In this case we might fasten the convex-edged piece of cardboard face to face with a second piece of cardboard, so that the two pieces would be at slightly different levels, and a small hole for the pencil point might be made through this second piece at the position corresponding to P. The curve might then be rolled, as in the former case, along the straight edge, and the path of P traced out as before.

Since

$$r=\sqrt{p^2+\left(\frac{p}{f(p)}\right)^2},$$

it will be observed that r becomes infinite for any value of p (or x) which makes $f(x)$ zero; unless x should also at the same time become zero, in such a way that the limit of $\frac{x}{f(x)}$ remains finite. It will therefore be necessary to exclude such points.

It will be observed that this limitation also prevents $\tan^{-1}\left(\frac{1}{f(x)}\right)$ from becoming infinite, since, in order to do so, $\frac{1}{f(x)}$ would require to pass from $-\infty$ to $+\infty$ and back again an infinite number of times; which would entail $f(x)$ becoming zero an infinite number of times.

Again, if for any value of x the integral $\int\frac{f(x)}{x}\,dx$ becomes infinite, then θ will become infinite and such a point must also be excluded.

We must also suppose that $f(x)$ and $\int \frac{f(x)}{x} dx$ are both continuous within the range of integration, in order that our rolling curve may be continuous.

General Method.

Suppose now that we wish to integrate

$$\int \mathrm{F}(x)\, dx,$$

where, for the range under consideration, $\mathrm{F}(x)$ is any twice differentiable function of x which is finite, single-valued and continuous; while $\mathrm{F}'(x)$ is also continuous.

We shall first take the case where $\mathrm{F}'(x)$ is not zero anywhere in the range.

We have

$$\int \mathrm{F}(x)\, dx = x\,\mathrm{F}(x) - \int x\,\mathrm{F}'(x)\, dx.$$

If therefore we write

$$x\,\mathrm{F}'(x) = f(x),$$

we have

$$\int \frac{f(x)}{x} dx = \mathrm{F}(x) + \text{constant};$$

and so the roulette method of integration may be applied directly to obtain $\int x\,\mathrm{F}'(x)\, dx$, which subtracted from $x\mathrm{F}(x)$ gives the required integral.

Writing x in place of p and employing inverse cotangents in place of inverse tangents, the equations giving θ and r for the rolling curve then become:

$$\left.\begin{aligned} \theta &= \mathrm{F}(x) + \cot^{-1}(x\mathrm{F}'(x)) + \mathrm{K}, \\ r &= x \sec\{\cot^{-1}(x\mathrm{F}'(x))\}. \end{aligned}\right\}$$

When this curve is rolled along the axis of y, its pole will trace out the curve

$$y = \int x\mathrm{F}'(x)\, dx.$$

The restrictions placed upon $\mathrm{F}(x)$ and $\mathrm{F}'(x)$ enable us to construct the rolling curve without θ or r becoming discontinuous or infinite.

The restriction that $\mathrm{F}'(x)$ should not be zero is, however, a serious one, which it is desirable to remove.

Now, provided that $F'(x)$ has either a finite lower limit or a finite upper limit for the range, it will always be possible to select some constant C, positive or negative, such that for the range of x under consideration the function

$$F'(x)+2C$$

is always of one sign.

Then we have

$$\int F(x)\,dx = xF(x)+Cx^2-\int x(F'(x)+2C)\,dx.$$

Thus if we write

$$x(F'(x)+2C) = f(x),$$

we have

$$\int\frac{f(x)}{x}dx = F(x)+2Cx+\text{constant};$$

and accordingly we may apply the roulette method and obtain

$$\int x(F'(x)+2C)\,dx,$$

which, subtracted from $xF(x)+Cx^2$, gives the required integral.

The equations giving θ and r now become:

$$\left.\begin{aligned}\theta &= F(x)+2Cx+\cot^{-1}\{x(F'(x)+2C)\}+K,\\ r &= x\sec[\cot^{-1}\{x(F'(x)+2C)\}].\end{aligned}\right\}$$

The simplest method of tracing this rolling curve is apparently (as in figure) to take a point P and a prime vector through it, from which an angle ω is measured such that

$$\omega = F(x)+2Cx.$$

A length $PN=x$ is then taken along this direction * and a perpendicular drawn to it through N.

---

* The projection of PN on the prime vector is obviously

$$x\cos\omega = x\cos\{F(x)+2Cx\}.$$

If we have a table of cosines of angles in radian measure, this enables us to construct the point N very simply on squared paper, without any direct measurement of angles.

Tables of cosines and sines of angles expressed in radian measure have been published by Dr. Carl Burrau (Berlin: Georg Reimer, 1907). In his preface he states (strangely enough) that this is the only table of this kind which has been published.

A point T is then taken on this perpendicular such that

$$\mathrm{NT} = \frac{1}{\mathrm{F}'(x)+2\mathrm{C}};$$

this length being measured off in the direction indicated in the figure, provided that $\mathrm{F}'(x)+2\mathrm{C}$ is positive.

The aggregate of points such as T is the rolling curve required.

The rolling curve may also be plotted directly in cartesian coordinates: ξ, η, with the point P as origin and the direction from which ω is measured taken as the direction of ξ negative.

If the system be such that the axes of ξ and η may be brought into coincidence with the axes of x and y respectively by motion in their own plane, we have obviously:

$$\left.\begin{aligned}\xi &= \frac{\sin(\mathrm{F}(x)+2\mathrm{C}x)}{\mathrm{F}'(x)+2\mathrm{C}} - x\cos(\mathrm{F}(x)+2\mathrm{C}x),\\ \eta &= \frac{\cos(\mathrm{F}(x)+2\mathrm{C}x)}{\mathrm{F}'(x)+2\mathrm{C}} + x\sin(\mathrm{F}(x)+2\mathrm{C}x).\end{aligned}\right\}$$

This method of integration possesses the great practical advantage of giving the integral for a whole range of values of the variable in one process, and should thus prove very useful in connexion with many physical investigations where the knowledge of how a function varies over a range is required without extreme accuracy.

On the other hand, the method is probably not very well adapted for use when the analytic form of the function is unknown since, in order to construct the rolling curve in the general case, we require not only the values of $\mathrm{F}(x)$ but also of $\mathrm{F}'(x)$.

Use of Curvimeter.

The results above obtained may be utilized in a somewhat different manner in effecting the graphical integration of functions.

In the roulette curve

$$y = \int x(\mathrm{F}'(x)+2\mathrm{C})\,dx$$

we may clearly put

$$y = s - \frac{1}{\mathrm{F}'(x)+2\mathrm{C}},$$

where s is the length (paying due regard to sign) of the portion of the rolling curve involved in the integration. Thus we get :

$$\int F(x)\,dx = xF(x) + Cx^2 + \frac{1}{F'(x)+2C} - s + \text{constant.}$$

The length s may be measured very accurately with a curvimeter or map-measurer, and the value of the integral may thus be obtained without cutting out the rolling curve.

This method may very likely be preferred to that first described, especially if the form of the rolling curve be complicated.

The most satisfactory form of curvimeter for this purpose appears to be the simple type, consisting of a small serrated wheel turning on a screw axle, which, after tracing out the curve to be measured, is run back to its initial position along a graduated scale, thus giving the length of the line required.

It is to be noted, in using this method, that the length of any portion of the rolling curve in which the curvature is reversed at a turning point is to be regarded as negative.

In case $F'(x)$ is not zero anywhere in the range of integration, we have :

$$\int F(x)\,dx = xF(x) + \frac{1}{F'(x)} - s + \text{constant.}$$

Since in this case $F(x) = \omega$, we see that $xF(x)$ is the length of the circular arc described with radius x and angle ω ; an since $\frac{1}{F'(x)}$ is the length of the portion NT of the tangent line to the rolling curve, we may, if we so desire, measure off

$$xF(x) + \frac{1}{F'(x)} - s$$

directly with the curvimeter and so obtain $\int F(x)\,dx$.

XCVII. *Emission Band Spectra of Aromatic Compounds.—Part I. Their Connexion with Infra-Red Absorption Bands and a Classification.* By JOSEPH KENNETH MARSH, *D.Sc.* (*Senior Assistant in Chemistry, the Queen's University of Belfast*) *.

[Plate X.]

THE work in which the writer has been taking a part for the last two years has furnished data with regard to the fluorescence and Tesla-luminescence of a considerable number of the simpler organic substances which are available for examination by these methods (J. Chem. Soc. cxxiii. pp. 642, 817, 2147, 3315 (1923), cxxv. pp. 418, 1743, 2123, (1924); J. Am. Chem. Soc. xlvi. p. 1351; Phil. Mag. xlviii. p. 628 (1924)). The examinations have been conducted upon substances in the vapour state, in which phase greater freedom is obtained for the molecules or their components to vibrate to their natural frequencies, with the consequence that spectra often result showing a much finer structure than those obtained from solutions. Wherever any considerable spectral structure has been observed, it has been found to possess no small degree of regularity, and the object of this paper is to classify the spectra studied, and in the following paper an attempt will be made to give an explanation of their characteristics. Whilst chief emphasis will be laid on emission spectra, when data of the vapour absorption are available use will be made of them, and it will be seen that they lend further evidence to the conclusions arrived at.

The inter-relationship of spectra in the ultra-violet and visible regions with those in the infra-red, forming the basis of Baly's theory of light absorption and fluorescence (Phil. Mag. xxvii. p. 632 (1914), xxix. p. 223 (1915); xxx. p. 510 (1915); xxxi. pp. 417, 512 (1916); xl. p. 1 (1920)), and worked out in some detail by Henri in his book 'Études de Photochemie,' will be further demonstrated. These writers find that the frequency differences between absorption or fluorescence bands are in a number of instances very nearly equal to the absolute frequency of an infra-red band of the same substance, and so regard the former bands as multiples or overtones of the latter. Owing to the fact that emission spectra appear to be very regular, it seems possible to classify them all into a comparatively few types, and to trace the causative agent determining each type. Nevertheless, it must not be thought that these emission spectra lack individual character, for it is very unusual to find two substances of which the spectra cannot be distinguished readily. A good example of each type of spectrum is reproduced in Plate X.

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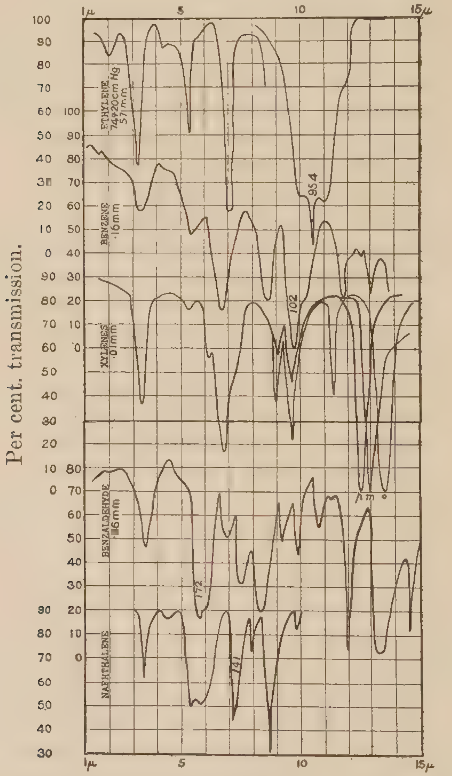
* Communicated by the Author.

TYPE I.—THE BENZENE SPECTRUM. (Pl. X. fig. I.)

Benzene as vapour exhibits series of narrow bands of absorption or fluorescence, the wave-numbers of the former differing from series to series by 92·1 units (Henri, *J. Phys. Rad.* 6, iii. p. 191) and of the latter by 99 units or thereabouts. In addition, the phosphorescence of benzene exhibits bands at regular intervals of the same dimensions, the average being 100 units (Kowalski, *Phys. Zeit.* xii. p. 956 (1912)).

Fig. 1.

Infra-red absorption spectra of typical compounds (after Coblentz and Spence).



Both Baly and Henri consider all these bands to be multiples of the great infra-red band of benzene at 9·8 μ or $1/\lambda$ 102 (Coblentz, 'Investigations of Infra-Red Spectra,' Carnegie Publication No. 35, 1905: see fig. 1 drawn from his curves). For the present we may conclude that the characteristic of the benzene type of spectrum is a succession of bands at intervals of 92 to 100 units; but besides this there is another series at intervals of about 16 units.

TYPE II *a*.—THE ALIPHATIC SUBSTITUENT TYPE. (Fig. II *a*.)

As typical of the spectra of a number of aliphatic substituted derivatives of benzene, that of *p*-xylene may be considered.

p-*Xylene* has, according to Mies (*Zeit. wiss. Phot.* vii. p. 357 (1909)), its chief absorption bands as under. (The figures represent (absolute frequencies) × 3 × 10^{-11}.) The frequency intervals are given in italics.

4186 4146 4109 4066 4028 3987 3948 3908 3869 3830 3792
40 *37* *43* *38* *41* *39* *40* *39* *39* *38* *39*
80 *79* *79* *78* *77*
3753 3710 3673 3627 3591
43 *37* *46* *36*
80 *82*

The Tesla-luminescence heads may be arranged thus:

3671 *83* 3588 *38* 3550 *45* 3505 *37* 3468 *45* 3423 *38* 3385
3660 *81* 3579 *38* 3541
3652 *85* *81* 3486
3642 *85* 3557
3605

Kowalski's phosphorescence bands do not appear to show much regularity, but Goldstein's observations of the cathodo-luminescence (*Verh. d. deut. Phys. Ges.* xiv. pp. 33, 493 (1912)) seem to exhibit great uniformity, though his measurements were only made to three significant figures. The following table constructed from his figures shows that the character of the bands is uniform with that of absorption and fluorescence.

2123 2079 2045 2000 1961 1923 1880 1842 1802 1764
44 *34* *45* *39* *38* *43* *38* *40* *38*
78 *84* *81* *78*

A difference of about 40 units is found to be the regular interval. Now, this corresponds to the frequency of a band at 25μ which is beyond the limit to which observations have been carried; but a difference of 79, or approximately twice the above, would indicate a band at $12{\cdot}6\mu$; and this is just the point at which the strongest band in the p-xylene infra-red spectrum is found (see fig. 1). We shall describe other spectra presently to show that p-xylene is typical of a group, and also how intimately the ultra-violet bands are related to the infra-red.

TYPE II *b*.—THE TESLA GREEN GLOW. (Pl. X. fig. II *b*.)

A number of aliphatic substituted benzene compounds have been observed to give a characteristic green glow under the Tesla discharge. The spectroscopic examination of this shows that it usually consists of two heads which have a frequency difference of 160 units. The best example of this type is hydrindene where the two bands occur at $1/\lambda$ 2119 and 1959. They are also found in indene, in p-cymene (one only), in cumene and tetrahydro-naphthalene (but not in naphthalene), and occur in the same positions. It is obvious that they are associated with heavy aliphatic side chains, and the frequency difference supports this conclusion, being just double or quadruple of the differences found for similar substances in the ultra-violet. A corresponding infra-red band is of frequent occurrence at $6{\cdot}2\,\mu$ ($1/\lambda$ $161{\cdot}3$) in benzene derivatives, though not in aliphatic compounds. The green glow was also observed visually in certain other substances besides those mentioned above, but was not sufficiently strong to photograph. The spectral analysis of the green glow of p-xylene differed notably from that of other substances. It contained a number of bands at closer intervals than those mentioned in the instances already given. These still show the ordinary p-xylene constant difference of about 40 units. The positions of the bands were $1/\lambda$ 2206 2168 2127 2104 2081 2039. The third and last two are probably identical with the three most refrangible bands of the cathodo-luminescence spectrum. Feeble photographic action is detectable down to $1/\lambda$ 1850, *i.e.* throughout most of the cathodo-luminescence region.

Having arbitrarily established these types, the grounds for doing so may be indicated by reference to the spectra of a number of other substances. Many of these will be found to possess characteristics showing that the individual spectrum may be a mixture of types.

Toluene.—The Tesla or ordinary vapour fluorescence shows bands which with almost equal validity may be arranged into series of 100 or of 80 unit intervals, as shown in the tables herewith.

3749	3647	3546	3442		3749	3669	3589
3731	3629	3529			3744	3660	
3713	3609			or	3731	3647	3566
3686	3589				3713	3629	3546
3669	3566	3465					

Maximum interval		104.	84
Minimum	,,	97.	80
Average	,,	101·5.	82

These and subsequent arrangements are not made arbitrarily, but with due care to classify the bands as naturally as possible according to their actual appearance on the photographic plates. There are also a few other minor bands which, however, stand alone in either classification and so have been omitted. It will be recognized at once that both the aliphatic derivative and the parent benzene types of spectrum are here present. In the infra-red, Coblentz found bands at 12·03 μ ($1/\lambda$ 83·1) and 9·73 μ ($1/\lambda$ 102·8), though neither is particularly strong.

Ethyl Benzene.—Both the vapour fluorescence and absorption are very blurred in character. Again, arrangement of the bands to conform to either type is permissible.

	3669	3569		3689	
3749	3649	3550	3749	3369	3588
3721				3649	3569
3689	3588		3721		3550

Intervals:—

max. 101, min. 100, av. 100·3; max. 82, min. 80, av. 81.

Mesitylene.—The four bands observed in the Tesla-luminescence spectrum can be paired to give intervals of 97 and 99 units. Thus the benzene type is dominant. The benzene bands are also prominent in the infra-red spectrum. (Coblentz, *loc. cit.*)

p-*Cymene.*—The Tesla-luminescence spectrum contains the following bands, which appear to mark the heads of coalesced groups.

3690 *81* 3609 *43* 3566 *43* 3523 *40* 3483

The last three are very indefinite, but it is evident that the recurrent interval is 81 or else about the half of this value, and therefore that the spectrum is of Type II. It will be remembered that the green glow is also found. In the infrared Coblentz observed a very deep band at 12·25 μ ($1/\lambda$ 81·7).

Phenol and Anisole.—These two substances gave a number of fluorescence bands, which were arranged according to the benzene type.

Phenol.

3581	*103*	3478	*95?*	3383?
3571	*99*	3472		
3553	*103*	3450	*95?*	3355?
3533	*104*	3429	*108?*	3321?

Anisole.

3639	*99*	3537
3612	*98*	3514
3605	*103*	3502
3576	*102*	3474

Other phenols and phenolic ethers gave almost continuous spectra, so do not lend any help to the present argument.

m-*Xylene.*—Coblentz' study of the infra-red spectra of the three xylenes showed them to have in this region very similar spectra, but the very intense band which occurs at about 13 μ has for each a slightly different position. From what has already been said it appears that the band in this region in the case of *p*-xylene dominates the whole of the spectra observed. If the corresponding band of *m*- and *o*-xylene is also dominant, the spacing of the ultra-violet bands in the three isomers should show variations to correspond with the varying frequency of this infra-red band. The frequencies and intervals of all the bands observed in *m*-xylene are tabulated below.

3741	3697	*75*	3622			3550?
	3687	*71*	3616			
	3678					
	3671	*75*	3696	*75*		3521
	3663					
	3645	*76*	3669			

A good regularity at intervals of about 75 units is shown.

o-*Xylene.*—The fluorescence spectrum is continuous in character, but shows one head and four fairly sharp bands, 1/λ 3731 3722 3655 3650. These may be paired to show differences of 74 units each.

The following table in connexion with the three xylenes is instructive, and affords striking evidence of the closeness of the relationship of the infra-red bands and the systems found in the ultra-violet.

Substance.	Chief infra-red band.		Av. interval of U. V. bands.
	μ.	ν.	ν.
p-xylene......	12·6	79·4	81
m-xylene......	13·0	76·9	75·2
o-xylene......	13·6	73·5	74

p-*Toluidine* (Pl. X. fig. III.).—Of a number of fluorescence spectra of amines examined, aniline and *p*-toluidine were the only ones which showed any banding. In the *p*-toluidine spectrum there are some eight or nine bands, most of them double, at intervals of about 42 units. Thus the spectrum bears a resemblance to that of *p*-xylene though occurring at greater wave-lengths, and the only structural difference is the attachment of a group weighing 15 in one instance and 16 in the other. In the infra-red the aromatic amines show strong characteristic bands at 6·1–6·15 μ and at 12·2–12·3 μ. Ammonia has a very strong band at 6·1 μ and a deep narrow one at 12·3 μ (1/λ 81·3), very similar in position to the characteristic bands of the xylenes, and probably the *p*-toluidine bands may be ascribed to this cause.

Indene resembles toluene and ethyl benzene in having an ultra-violet spectrum of mixed types, though here the aliphatic is perhaps the better developed.

Indene Bands.

3597	*76*	3521	*79*	3442	*72*	3370		3597	*102*	3495	*103*	3392
3590	*75*	3515	*77*	3438				3590	*101*		*100*	3389
3584	*75*	3509					or	3584				
3570	*75*	3495						3570	*100*	3470	*100*	3370
		3470	*78*	3392						etc.		
		3463	*74*	3389								

Hydrindene has, besides the green glow already mentioned, other bands in the ultra-violet of the type found in aliphatic substituted benzene derivatives.

Hydrindene Bands.

3701			
3690	*76*	3614	*47*
		3607	
3675	*77*	3598	
		3585	

Phenyl Acetylene.—The Tesla-luminescence bands show a resemblance to benzene.

3588	*51*	3535	*102*	3435			
3570	*45*	3525	*99*	3426	*104*	3322	
3540	*52*	3488					3190

Styrene.—The Tesla spectrum is distinctly of the benzene type, though not a large number of bands are seen.

3490	3482	3475	3459	3453	3413	3407
		98	*102*	*98*	*102*	
		3377	3365	3355	3311	

This might be expected, for neither this substance nor the last has a true aliphatic group, and the band at about 10 μ in benzene is also very strong in ethylene; in fact, it seems not improbable that this infra-red band is a characteristic of a carbon atom with only three valencies satisfied rather than of a benzene nucleus. This subject will be discussed further in the following paper.

The *Methyl Naphthalenes* gave a Tesla spectrum in the red region which appears to be the naphthalene counterpart to the green glow of aliphatic derivatives of benzene. Just as the previously known spectra of naphthalene occur at greater wave-lengths than in benzene, so also does this newly-observed glow. The highest frequency head of naphthalene vapour fluorescence is at $1/\lambda$ 3245, and the first head of the green glow at 1705, whereas the benzene fluorescence spectrum begins at 3749, and the green glow of derivatives at 2119. The interval in the former case amounts to 1500 and in the latter to 1630. No corresponding glow has been observed in anthracene derivatives. The first strong ultra-violet fluorescence head is at 2758, and it will be found on calculation that an interval of similar dimensions to that obtaining between the ultra-violet and visible heads in benzene or naphthalene and their derivatives would indicate a wave-length for the glow of anthracene lying in the infra-red.

TYPE III.—THE BLUE BANDS. (Pl. X. fig. V.)

A considerable number of substances examined for Tesla-luminescence have given a blue spectrum which consists of a number of bands, but is chiefly characterized by three of great strength at regular intervals of 173 units of frequency. This spectrum is not excitable to more than a slight extent, if at all, by light.

Benzaldehyde is the outstanding example of the type, and may be considered first. The absorption spectrum consists of three bands at $1/\lambda$ 4098 3565 3049 respectively (Steiner, *Comp. Rend.* clxvi. p. 744 (1913)) showing intervals of 516 and 533. The first blue band is at 2519, an interval from the nearest absorption band of 530, without making allowance for passing from measurements in solution to those in vapour. The other blue bands of the series are at $1/\lambda$ 2346 2175 2004, the four having average intervals of 172·3, and in the infra-red there is a strong band at 5·84 ($1/\lambda$ 171·2). It will be seen that the intervals between the absorption bands are approximately three times those between the blue bands.

Except in the case of acetophenone and anisaldehyde, where in place of the usual comparatively sharp bands a much more diffuse spectrum is found, the blue bands of all the substances examined are very similar in position and appearance apart from intensity. Moreover, they lie in a region by themselves, and so are not found superposed on other types, though they may be accompanied by them.

An interesting variation was found in the case of benzoquinone. This substance gave a yellow glow under the Tesla discharge, and the following bands were observed :—

1872 1699 1623 1564 1534

The first two and the last were strong, and show intervals of 173 and 165 units. Considering the small accuracy with which measurements could be made with the quartz spectroscope in this region, agreement with the usual interval of about 173 units would seem to be maintained.

TYPE IV.—THE CONDENSED NUCLEI. (Pl. X. fig. IV.)

As an example we shall take *Anthracene*, the Tesla-luminescence of which is in the most sensitive photographic region and is of exceptional intensity, a few seconds sufficing to photograph it. Several bands are seen ; they occur at $1/\lambda$ 2882 2758 2618 2465 2326. The intervals between the last four are respectively 140 143 139 units. The absorption spectrum has bands at 2654 2796 2938 3076, the respective intervals being 142 142 138. The same interval as in emission is here evident. The infra-red spectrum has not been studied with success, and the most nearly related substance of which the spectrum has been mapped in this region is naphthalene.

Naphthalene.—The fluorescence bands recorded by Dickson (*Zeit. wiss. Phot.* viii, p. 247 (1910)), fourteen in number, show a perfectly regular spacing at intervals of 47 units. A cursory examination of naphthalene fluorescence in chloroform solution made by Mr. W. H. McVicker showed seven or eight of these bands, and moreover gave grounds for stating that every third one was stronger than its neighbours—*i. e.*, there is also a regularity at intervals of 141 units, as in anthracene. The vapour-emission spectra of naphthalene do not show narrow banding. This is the only instance yet found where the vapour gives rise to a less detailed spectrum than the solution. In a recent study of naphthalene vapour absorption, Henri and Làszlò (Proc. Roy. Soc. A, cv. p. 662 (1924)), find the same interval of 47·4 units between many of the chief bands as is found in solution fluorescence.

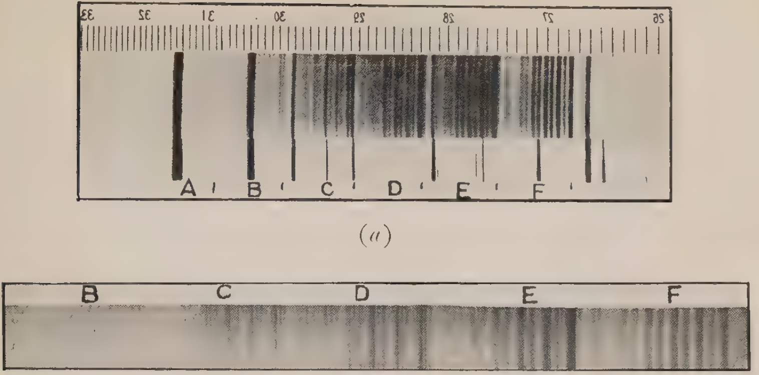
The infra-red spectrum of naphthalene has been examined by Stang (Phys. Rev. ix. p. 542 (1917)), and shows a strong band at $7{\cdot}19\,\mu$ ($1/\lambda$ 139·1). Many of the benzene bands are also found, but the band at 7·19 is among the strongest, and persists in most of the simple derivatives which he examined. There can be little doubt that this band is characteristic of naphthalene, and probably of anthracene and other nuclei also. Numerous anthracene derivatives have recently been examined, and their Tesla-luminescence spectrum usually shows as the main feature the anthracene bands, but often with slight variations in position. Octahydroanthracene and tetrahydronaphthalene are interesting derivatives which have been studied. In both cases the spectral character has reverted to Type II., the aliphatic substituted benzene type.

Besides the substances which it has been possible to place in one of the classes enumerated in the preceding pages, there are very many which give only continuous spectra. Certain groups prevent emission spectra from developing at all, and of the rest some more than others tend towards the production of continuous spectra, but with increasing complexity a stage of complete continuity is always soon reached. Probably in no substance examined are there less than two superimposed types of oscillation. Further study will reveal the theoretical significance of the present classification, but this is deferred to the following paper.

Abstract.

The paper is largely a commentary on previous work by the author and collaborators. The spectra studied are shown to be capable of classification into :—(1) A benzene type, characterized by bands at frequency intervals of 102 and 15·9 waves/mm. (2) A benzene aliphatic-derivative type with band intervals of 40 or 80 in the ultra-violet. These substances under the Tesla discharge also usually give a green glow consisting of two bands at an interval of 160. (3) "The Blue Bands"—a spectrum produced by the Tesla discharge through a number of substances of which benzaldehyde is an outstanding example, characterized by three very strong bands at intervals of 172 units. (4) A condensed nuclei type, perhaps not so well established. Anthracene and derivatives show three or four characteristic bands near 4000 Å.U. at intervals of 142 units, whilst naphthalene has a series of bands at one-third of this interval. Many substances do not give any emission, or only one of a continuous character, and so cannot be classified. It is shown that in the infra-red, bands of absolute frequency equal to the above ultra-violet frequency differences are in each case well marked and characteristic.

FIG. I.



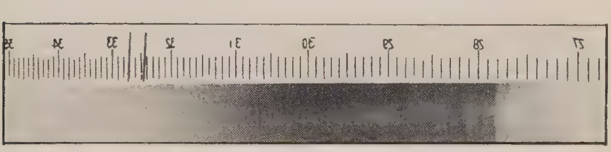
(a)

(b)

The Benzene Spectrum. TYPE I.

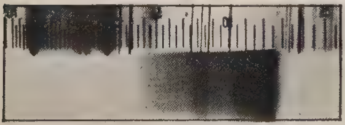
(a) Fluorescence spectrum (with Hg lines).
(b) Tesla-luminescence, large spectroscope without enlargement.

FIG. II *a*. TYPE II *a*.



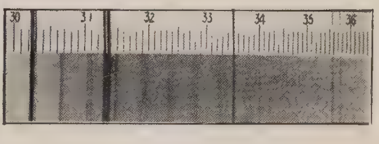
p–Xylene.

FIG. II *b*. TYPE II *b*.



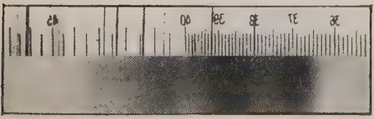
Hydrindene (visible region only).

FIG. III.



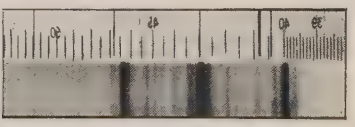
p–Toluidine.

FIG. IV. TYPE IV.



Anthracene.

FIG. V. TYPE III.



Benzaldehyde.

Typical Emission Spectra.

Enlargements to nearly double size.

XCVIII. *Quantum Magnetic Tubes in Rotation.*

By H. Stanley Allen, *M.A., D.Sc., Professor of Natural Philosophy in the University of St. Andrews*[*].

QUANTUM Theory requires an atomicity in nature of a kind not previously suspected[†]. It is probable that this atomicity is intimately related to the existence of positive and negative electrons, a fact which is not as yet satisfactorily explained. It has been shown in earlier papers[‡] that the theory of quanta suggests the existence in three dimensions of discrete tubes of magnetic induction, corresponding to the "magnetic lines" which Faraday conceived of as physical entities, or in four dimensions of discrete electromagnetic tubes of force, the "calamoids" of Prof. E. T. Whittaker[§]. It is the object of the present communication to discuss the properties of quantum magnetic tubes rotating about an axis, to determine their angular momentum and energy, and to consider the electrostatic field set up by their rotation and the possible connexion between such a rotating tube and an electron. It may be said at the outset that the paper is frankly speculative in character.

§ 1. Magnetic Tubes in Rotation.

Towards the end of 1920 Professor E. T. Whittaker drew my attention in conversation to the nature of the electrostatic field which would be set up by magnetic tubes in rotation. He pointed out that if a set of magnetic tubes, such as would be produced by a small current circuit, or a small magnet, could be supposed to rotate like rigid wires about the axis of symmetry, an electric field would be produced which in the equatorial plane would vary inversely as the square of the distance from the centre of the system.

A large number of such systems oriented at random would produce, on the average, an electric field at a distance similar to that due to an electrostatic charge, that is, a field varying inversely as the square of the distance. The "equivalent" electrostatic charge for a single system would be proportional to the magnetic moment (M) of the elementary magnet, and the angular velocity (ω) with which the system is rotating.

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[*] Communicated by the Author.

[†] J. H. Jeans, 'Report on Radiation and the Quantum Theory,' Chapter 8.

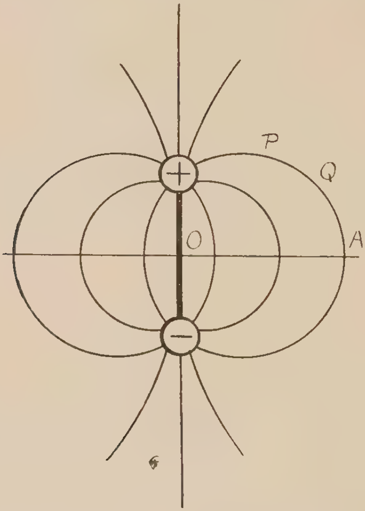
[‡] H. S. Allen, Phil. Mag. xlii. p. 523 (1921), xlviii. p. 429 (1924); Proc. Roy. Soc. Edin. xlii. p. 213 (1922).

[§] E. T. Whittaker, Proc. Roy. Soc. Edin. xlii. p. 1 (1921).

Further, Whittaker drew attention to the remarkable fact that for a given direction of the axis of the magnet there were *two* possible directions of rotation for the magnetic tubes, thus suggesting the possibility of interpreting the difference between positive and negative electric charges.

An obvious difficulty in the way of applying this conception to the classical magnetic tubes associated with an elementary magnet lies in the fact that at a great distance from the magnet the tubes would be moving with a velocity

Fig. 1.



exceeding the velocity of light. This difficulty, however, does not arise if we adopt the view now advocated of the existence of discrete quantum tubes, for we need consider the rotation of only a limited number of such tubes, or even that of a single quantum tube. Thus we may in imagination isolate a single quantum tube, such as the one indicated in fig. 1 passing through the points P and Q, and discuss the electric field associated with that particular tube, the velocity of P being less than that of light, even in the limiting case in which the velocity of the point A in the equatorial plane approaches the velocity of light.

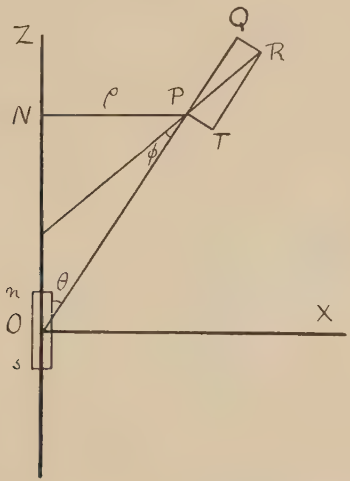
At this point an interesting comparison is suggested between the rotation of such quantum tubes and the rotation of an electron in one of the circular orbits in Bohr's theory.

We know that in that theory an orbit with a large value for the quantum number corresponds to a velocity less than the velocity of light. Also an important question is suggested as to the greatest distance at which electrostatic effects have actually been observed. In the classical theory it is always assumed that the field of an electric charge extends to infinity, but it would be interesting to know what experimental evidence there is bearing on this point.

§ 2. A QUANTUM MAGNETIC TUBE IN ROTATION.

We consider a single quantum tube such as would originate in a small magnet of magnetic moment M, and suppose it to be rotating with angular velocity ω about the axis of the magnet. Let A be the area of cross-section, ds the length of an element of the tube at any point P, determined by the coordinates r, θ.

Fig. 2.



The mass associated with each unit of volume of a magnetic field[*] is $KB^2/4\pi$, consequently the mass of an element of the tube at P is $\dfrac{KB^2}{4\pi}A\,ds$. Draw a perpendicular PN from P to the axis of the magnet, and let the length of

[*] In this paper the electric and magnetic coefficients K and μ will be retained in the analysis.

this perpendicular be ρ. Then the angular momentum of the element about the axis is $\frac{KB^2}{4\pi}A\,ds \times \rho^2\omega$. Now for a quantum tube the flux of magnetic induction, $BA = \mu HA = h/e$, and is constant along the tube. Therefore the angular momentum reduces to

$$\frac{K\mu}{4\pi}\cdot\frac{h}{e}\cdot\omega\,.\,H\rho^2 ds.$$

The angular momentum for the whole tube is found by integrating this expression throughout the length of the tube.

Evaluation of the Integral $\int H\rho^2 ds$.

The strength, H, of the magnetic field at P may be found by resolving the magnetic moment, M, along and perpendicular to OP. Thus we find that the field at P is made up of two components in these two directions. The former component, that is the component represented by PQ in the diagram, is given by $\frac{2M\cos\theta}{\mu r^3}$; the latter component is $\frac{M\sin\theta}{\mu r^3}$, represented in the figure by the line PT perpendicular to OP, so that the resultant magnetic field, H, is represented by PR.

Thus
$$H = PR = \sqrt{(PQ^2 + PT^2)}$$
$$= \frac{MR}{\mu r^3}\sqrt{(1 + 3\cos^2\theta)}.$$

The inclination of this resultant force to the line OP is $R\hat{P}Q = \phi$, where

$$\tan\phi = \frac{RQ}{QP} = \frac{PT}{PQ} = \frac{\sin\theta}{2\cos\theta} = \tfrac{1}{2}\tan\theta.$$

It is easily shown that

$$\sin\phi = \frac{\sin\theta}{\sqrt{(1 + 3\cos^2\theta)}}.$$

Now turning to the integral $\int H\rho^2 ds$ we have

$$\rho = r\sin\theta \text{ and } ds = r\,d\theta/\sin\phi,$$

and substituting in the integral we get

$$\begin{aligned}\int \mathrm{H}\rho^2 ds &= \int \frac{\mathrm{M}}{\mu r^3}\sqrt{(1+3\cos^2\theta)}\,r^2\sin^2\theta\,ds\\
&= \frac{\mathrm{M}}{\mu}\int_0^\pi \frac{\sqrt{(1+3\cos^2\theta)}\,\sin^2\theta\,d\theta}{\sin\phi}\\
&= \frac{\mathrm{M}}{\mu}\int_0^\pi (1+3\cos^2\theta)\sin\theta\,d\theta\\
&= -\frac{\mathrm{M}}{\mu}\Big[\cos\theta+\cos^3\theta\Big]_0^\pi\\
&= \frac{4\mathrm{M}}{\mu}.\end{aligned}$$

Substituting this value in our expression for the angular momentum, we find that the total angular momentum for the single quantum tube is

$$\frac{\mathrm{K}\mu}{4\pi}\cdot\frac{h}{e}\cdot\omega\cdot\frac{4\mathrm{M}}{\mu}=\frac{\mathrm{KM}}{\pi}\cdot\frac{h}{e}\cdot\omega.$$

We notice that the magnetic tube which we are considering has an equivalent moment of inertia

$$\mathrm{I}=\frac{\mathrm{KM}h}{\pi e}.$$

Remembering that the angular velocity, ω, can be expressed in terms of the frequency by writing $\omega=2\pi\nu$,

$$\text{the Angular Momentum}=\frac{2\mathrm{KM}h}{e}\nu.$$

The kinetic energy of the quantum tube is obtained by multiplying the angular momentum by $\frac{1}{2}\omega$, and so we find

$$\begin{aligned}\text{the Kinetic Energy}&=\frac{1}{2}\frac{\mathrm{KM}h}{\pi e}\omega^2 \text{ or } \tfrac{1}{2}\mathrm{I}\omega^2,\\
&=\frac{2\pi\mathrm{KM}h}{e}\nu^2.\end{aligned}$$

§ 3. ELECTROSTATIC FIELD OF A ROTATING TUBE.

When a magnetic tube is in motion, it produces an electric field. In the case of the rotating quantum tube already considered the electric field set up at a point A in the equatorial plane is equal to Bv, where v is the velocity of the rotating tube at that point. If the distance OA is a, the velocity $v = a\omega = 2\pi a\nu$, and thus the electric field is $\mathrm{B}a\omega$, or $2\pi a\mathrm{B}\nu$.

Let us assume that the electric field at A is the same as would be produced by an electrostatic charge E at the point O, and then determine the value of that charge. Since the two fields are assumed to be equal,

$$\frac{\mathrm{E}}{\mathrm{K}a^2} = \mathrm{B}v = \mathrm{B}a\omega = 2\pi a\mathrm{B}\nu.$$

Now the magnetic field at A is supposed to be due to an elementary magnet of moment M, so that the strength of the magnetic field is $\mathrm{M}/\mu a^3$. Thus at the point A,

$$\mathrm{B} = \mu\mathrm{H} = \mathrm{M}/a^3.$$

Hence

$$\frac{\mathrm{E}}{\mathrm{K}a^2} = \frac{\mathrm{M}}{a^3}v,$$

or, since $v = a\omega$,

$$\frac{\mathrm{E}}{\mathrm{K}a^2} = \frac{\mathrm{M}}{a^2}\omega.$$

Therefore we have

$$\frac{\mathrm{E}}{\mathrm{K}} = \mathrm{M}\omega.$$

Thus the *equivalent charge* at O is given by $\mathrm{E} = \mathrm{KM}\omega$.

This relation may now be used in expressing the angular momentum of the rotating quantum tube.

$$\text{Angular Momentum} = \frac{\mathrm{KM}}{\pi} \cdot \frac{h}{e} \cdot \omega$$
$$= \frac{\mathrm{E}}{e} \cdot \frac{h}{\pi}.$$

If we assume that the charge $\mathrm{E} = \mathrm{Z}e$, expressing the charge in terms of the electron charge e, then the Angular Momentum $= \mathrm{Z} \times h/\pi$.

The Kinetic Energy of the tube takes the simple form

$$\frac{1}{2}\frac{\mathrm{E}}{e} \cdot \frac{h}{\pi} \cdot \omega$$
$$= \frac{\mathrm{E}}{e} \cdot h\nu, \quad \text{since } \omega = 2\pi\nu,$$
$$= \mathrm{Z}h\nu.$$

If, in the above results, we take $\mathrm{Z} = 1$, so that the equivalent charge equals the electron charge e, we find for the angular momentum of the rotating tube h/π, and for the kinetic energy $h\nu$. It is important to observe that these values are exactly double those obtained by adopting Nicholson's quantum condition which postulates a natural unit of angular momentum of magnitude $h/2\pi$, corresponding to an amount of kinetic energy $\frac{1}{2}h\nu$. We have, in the present case, an amount of energy corresponding to Planck's quantum $h\nu$. We may compare the results we have obtained with those in the case of the simple Bohr atom, where the *kinetic* energy of the circulating electron is $\frac{1}{2}h\nu$ and the *potential* energy is numerically double this amount. It may be pointed out that in our present work we are virtually expressing potential energy in terms of what, from the ordinary standpoint, would be described as concealed kinetic energy.

§ 4. ELECTRONS REGARDED AS ROTATING TUBES.

It is instructive to take some numerical examples of these results.

Case I.—According to the principle of relativity the energy corresponding to a mass m as judged by an observer relatively at rest is mc^2. Let us assume that in the case of a negative electron this amount of energy may be identified with the energy of rotation of a single magnetic tube. This corresponds to the assumption made by Stark *, who identified the equivalent energy of an electron at rest with one quantum of energy $h\nu$. Then we have

$$h\nu = mc^2.$$

Taking

$$h = 6{\cdot}558 \times 10^{-27} \text{ erg sec.},$$
$$m = 9 \times 10^{-28} \text{ gm.},$$
$$c = 3 \times 10^{10} \text{ cm./sec.},$$

this yields for ν, the frequency of rotation, the value $1{\cdot}24 \times 10^{20}$ sec^{-1}. That is, a single quantum tube rotating with this frequency would have an amount of inertia equal to that of a negative electron.

The frequency in question may be expressed in a different way by using the fundamental Rydberg frequency

$$\nu_0 = \frac{2\pi^2 me^4}{h^3 K^2}.$$

Putting

$$\frac{2\pi e^2}{hcK} = \alpha,$$

where α is a pure number, we may write

$$mc^2 = \frac{2h\nu_0}{\alpha^2}.$$

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* Stark, *Phys. Zeitschr.* viii. pp. 881–884 (1907).

The form of this result suggests that the amount of the energy mc^2 associated with the mass of the electron may be regarded as a quantum of energy $h\nu$, provided $\nu = \frac{2\nu_0}{\alpha^2}$.

If we further assume that the maximum velocity of the rotating tube approaches the velocity of light, we can form an estimate of the size of our electron. This means that the velocity of the point A is supposed to approach the velocity of light, so that $v = a\omega = c$. Consequently, ω being $2\pi\nu$, $2\pi\nu a = c$, and thus

$$a = \frac{c}{2\pi\nu} = \frac{c}{\frac{4\pi\nu_0}{\alpha^2}} = \frac{\alpha^2 c}{4\pi\nu_0} = 3{\cdot}86 \times 10^{-11} \text{ cm.}$$

A more convenient expression for the radius is obtained in terms of the innermost orbit in Bohr's theory of the hydrogen atom. This may be written

$$a_1 = \frac{\alpha c}{4\pi\nu_0}.$$

Therefore $\qquad a = \alpha a_1.$

Assuming $e = 4{\cdot}774 \times 10^{-10}$ E.S.U. the numerical value for α is 1/137. The radius of the electron is 1/137 times the radius of this innermost orbit.

From the relation $E = KM\omega$ the magnetic moment of the elementary magnet is found to be

$$M = \frac{\mu h e}{2\pi m}.$$

This is twice the magnetic moment of the Bohr magneton, and it may be mentioned that it corresponds very closely with the value derived from the saturation intensity of magnetization of iron, which according to Ewing [*] is nearly 2×10^{-20} c.g.s. units per atom of iron.

The ratio of the angular momentum to the magnetic moment for the electron here considered has the value $2m/\mu e$, which is equal to the gyromagnetic ratio deduced from the theory of electron orbits by O. W. Richardson [†].

Case II.—In the preceding calculations we have neglected the energy associated with the frequency characteristic of the tube itself, energy which may correspond, possibly, to an internal vorticity. When this is taken into account we have to deal with an amount of energy $h\nu_r$ due to the rotation of the whole tube about an axis with frequency ν_r, and also an amount of energy $\frac{1}{2}h\nu_s$ which is due to the internal condition of the tube, and would be present in the tube when not rotating, ν_s being the frequency appropriate to the stationary tube*. These quantities are additive, and as there are two possible directions of rotation we have for the energy in one case $h\nu_r+\frac{1}{2}h\nu_s$, and in the other $h\nu_r-\frac{1}{2}h\nu_s$. As the first amount is clearly greater than the second, let us identify the first case with a positive electron, the second with a negative electron.

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[*] J. A. Ewing, Proc. Roy. Soc. Edin. xlii. p. 124 (1922).

[†] O. W. Richardson, Phys. Rev. xxvi. p. 248 (1908); Proc. Roy. Soc. cii. p. 538 (1923).

Let m_{P} be the mass of the proton (+ve electron), and m_{C} the mass of the corpuscle (−ve electron). Then, in accordance with the principle of relativity,

$$m_{\text{P}}c^2=h\nu_r+\tfrac{1}{2}h\nu_s$$

$$m_{\text{C}}c^2=h\nu_r-\tfrac{1}{2}h\nu_s.$$

That is to say, we have here expressions for the mass of the proton and the corpuscle expressed in terms of these two frequencies ν_r and ν_s. Dividing the first by the second we get at once

$$\frac{m_{\text{P}}}{m_{\text{C}}}=\frac{2\nu_r+\nu_s}{2\nu_r-\nu_s},$$

and therefore
$$\frac{m_{\text{P}}+m_{\text{C}}}{m_{\text{P}}-m_{\text{C}}}=\frac{2\nu_r}{\nu_s}.$$

The value found experimentally for $\frac{m_{\text{P}}}{m_{\text{C}}}$ is very nearly 1833 (Bucherer and Ladenburg). Using this numerical value we find $\frac{\nu_r}{\nu_s}=0{\cdot}50051$. This means that the frequency of rotation of our magnetic tube is rather larger than one-half the frequency characteristic of the stationary tube.

It is convenient, as in Case I., to express the frequency in terms of the fundamental Rydberg frequency

$$\nu_0=\frac{2\pi^2me^4}{h^3\text{K}^2}$$

by means of the relation

$$mc^2=\frac{2h\nu_0}{\alpha^2}.$$

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* H. S. Allen, Phil. Mag. xlii. p. 523 (1921)

From the equations we find without difficulty the results

$$\left.\begin{aligned} \nu_r &= \frac{\nu_0}{\alpha^2}\left(\frac{m_P}{m_C}+1\right) \\ \nu_s &= \frac{2\nu_0}{\alpha^2}\left(\frac{m_P}{m_C}-1\right) \end{aligned}\right\} .$$

Substituting the numerical values

$$\nu_0 = 3{\cdot}271\times 10^{15},\ 1/\alpha = 137,$$

we find

$$\left.\begin{aligned} \nu_r &= 1{\cdot}126\times 10^{23}\ \text{sec.}^{-1} \\ \nu_s &= 2{\cdot}250\times 10^{23}\ \text{sec.}^{-1} \end{aligned}\right\} .$$

If we assume, as in Case I., that $a\omega_r = c$, we find as a limiting value for a, the radius of the electron, $4{\cdot}24\times 10^{-14}$ cm. It should be noticed that on these assumptions the size of a negative electron does not differ from the size of a positive electron, the radius being a quantity of the same order of magnitude as was obtained by Rutherford, from experiments on the scattering of α particles, to represent the size of an atomic nucleus. The radius of the negative electron on the classical theory is well-known to be a quantity larger than this, but that estimate is derived from the assumption that the electron may be treated as a charged sphere.

Although no quantitative explanation has yet been found for the frequencies ν_r and ν_s, which have been assigned so as to give the masses actually observed, it may be suggested that they are in some way determined by the limiting condition that the velocity of the extreme edge of the rotating tube cannot exceed the velocity of light.

It is interesting to compare with the suggestions here made a surmise as to the relation between positive and negative electricity put forward independently by Sir Oliver Lodge * in his Presidential Address to the Röntgen Society on 6th November, 1923.

"Let us suppose then that round the nucleus of an atom the ether is in a state of violent rotation. It might even be suggested that a proton itself is always and constitutionally in a state of circulation at a speed comparable to the velocity of light, and that in this way its mass is accounted for, as distinguished from the much smaller mass of the electron, which presumably is not in a state of rotation. We might go so far as to surmise—as indeed we do for many other reasons, connected with the transmission of waves by a vortex filled medium—that the normal ether contains a constitutional rotation comparable to the velocity of light, and

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* Brit. Journ. of Radiology, vol. xx., Jan. 1924.

that upon this, when a pair of electric units are being somehow generated, two equal opposite rotations are superposed; one in opposition to the original rotation, giving a result slightly nearer to the velocity of light than before, conceivably sufficient to cause what would otherwise be the mirror-image of the negative electron to have a mass 1,850 times as big."

§ 5. DISCUSSION OF SUGGESTED ELECTRONIC AND ATOMIC MODELS.

In considering the model here put forward, attention may be drawn to a paper by H. Bateman *. He remarks that an electron rotating on its axis like a planet does not radiate as much as when not rotating. "The fact that the radiation is reduced by rotation may indicate that revolving electrons do rotate."

It will have been noticed that the fundamental electric charge here postulated possesses axial and not spherical symmetry. Further, it must possess magnetic as well as electric properties. In this connexion reference may be made to a paper by Duane †, in which a calculation is made of the velocity of projection of α particles on the assumption that atomic nuclei may be regarded as small magnets, the resulting velocity being of the order of magnitude observed experimentally. Reference may also be made here to the important work of Stern and Gerlach, who have deduced from their experiments the magnetic moment of the normal silver atom in the gaseous state as being one Bohr magneton. This magnetic moment is usually supposed to be due to what may be called the outer, or loosely bound electrons.

The picture of *an atomic nucleus* suggested by the foregoing considerations is that of a set of magnetic tubes rotating about a common axis with the same angular velocity, some of the tubes representing positive, the remainder—the smaller number—negative electrons.

Outside the nucleus we shonld expect to have in addition a set, or sets, of outer magnetic tubes, of larger size, rotating or capable of rotating about the same axis so as to give rise to the external magnetic and electric field due to the atom. These tubes may be supposed to rotate with very much smaller angular velocity than the inner set. For instance, they might have an angular velocity comparable with that of the radius vector to an electron in one of the Bohr orbits. In that case the mass to be associated with these outer tubes would be very small in comparison with the mass of the nucleus.

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* Nat. Acad. Sci. Proc. v. p. 367 (1919).

† Duane, Phys. Rev. v. p. 335 (1915).

According to the hypothesis advanced *each quantum tube may be regarded as a potential electron.* In a former paper [*] it was suggested that the emission of radiation consisted in, or was consequent upon, the liberation of a quantum tube from an atomic or molecular system. Taking this suggestion in connexion with the present hypothesis, some light is thrown on the remarkable reciprocal relation between radiation and electrons. With characteristic boldness Sir Oliver Lodge [†] discussed this problem in an address on Ether and Electrons, and suggested that the actual generation of an electron by means of light is not an altogether impossible idea.

Further, the results and suggestions of the present paper may be considered in relation to the "Quantum Mechanism in the Atom" described by Prof. Whittaker. For the magnetic wheel in rotation, used as an illustrative model, is equivalent to a set of rotating magnetic tubes, and the structure is essentially a mechanism by which an electrostatic field is produced by the motion of these tubes. Stress may be laid on Prof. Whittaker's argument that when an electron is approaching an atom, the electric field about the atom is not permanent, but is evoked by the approach of the electron. The electron induces within the atom a "magnetic current," *i. e.* the magnetic analogue of an electric current.

Also it is worthy of special note that in this mechanism the electric separation in the atom, which is caused by the collision with the bombarding electron, is precisely a separation of two electronic charges $+e$ and $-e$. The process might be described as the manufacture of a positive and negative electron, or at least as a stage in such manufacture. Again, the emission of radiation by the mechanism may be regarded as the liberation of a magnetic tube from the structure.

"Until fuller certainty comes, it is well that every hypothetically possible line of advance should be explored" [‡]. The suggestions of this paper are put forward in the conviction that these words are in a special sense true at the present stage in the development of physical theory.

The University,
St. Andrews,
6 March, 1925.

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[*] H. S. Allen, Phil. Mag. xlviii. p. 429 (1924).

[†] Sir Oliver Lodge, 'Nature,' cxii. p. 185, August 4th, 1923.

[‡] W. Peddie, Proc. Roy. Soc. Edin. xlii. p. 223 (1922).

XCIX. *A Space Charge Effect.* *By* E. W. B. Gill, *M.A., B.Sc., Fellow of Merton College, Oxford* *.

1. If in a 3-electrode gas-free valve the grid and plate are both maintained at a positive potential with regard to the filament, the grid potential being the higher, then when the filament is heated, the electrons which leave it move towards the grid, some are collected on the grid, and the remainder pass through it and are collected on the plate.

If the plate potential is only a few volts, and if n_1 is the number of electrons reaching the grid per second, n_2 the number reaching the plate, it is found in general that the ratio $\frac{n_1}{n_1+n_2}$ is constant if n_1+n_2 is varied, this last being the total number leaving the filament, which is controlled by the filament temperature. That is, a fixed proportion of the current from the filament reaches the plate.

Thus with a Mullard Valve in which the grid was kept at 40 volts and the plate at 6 volts (the negative end of the filament being taken as zero potential), the following results were obtained, the currents being measured in milliamperes:

Total emission from filament ……	2·5	5	7·5	10	15	20
Current received by plate………..	1·3	2·6	4·0	5·3	7·9	10·6

while with the plate at 10 volts and the grid still at 40, the results were :

Total emission …………	2·5	5	7·5	10	15	20
Plate current ……………	1·4	2·7	4·1	5·5	8·2	10·9

In the first case the plate received 53 per cent. of the total emission, the grid receiving the other 47 per cent., these proportions being independent of the emission. In the second case the plate received a slightly higher proportion, 54·5 per cent. of the total.

The total current n_1+n_2 passing across the valve cannot be increased beyond a certain limit, which is reached when the space charges and the fixed potentials together make the electric force zero at the filament, as in Langmuir's well-known calculations.

2. The Mullard valve used had a cylindrical grid of diameter about 4 mm., the plate being a cylinder of 1 cm. diameter. If the above experiment be tried with a valve in which the plate is a good deal larger in diameter than the

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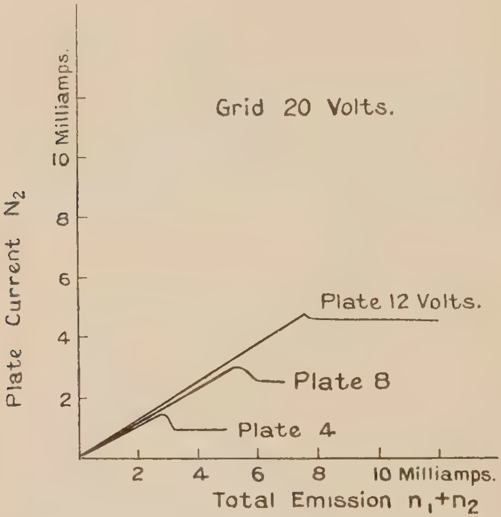
* Communicated by Professor Townsend.

grid, the results are entirely different. The valve used in the experiments to be described was made by the Marconi Company, and had a grid of 5 mm. diameter, and a plate of 2·5 cm. diameter. Thus the ratio of plate diameter to grid diameter, which in the Mullard valve was 2·5, was 5 in the Marconi valve.

The filament was electrically heated to various temperatures by varying the potential across it from about 4 to 6 volts. The results obtained are shown in figs. 1, 2, 3. The three curves in fig. 1 represent the results of experiments with the grid at 20 volts and the plate at 4, 8, and 12 volts, the ordinates being the current n_2 to the plate and the abscissæ the total current n_1+n_2. The curves in fig. 2 represent the results of experiments which were done exactly under the same conditions, except that the grid was at 30 volts, while in fig. 3 the grid was at 40 volts. (It should be noted that the plate potentials are so low that the effect of secondary emission from the plate is negligible.)

Fig. 1.



If the results for the Mullard valve were plotted in the same way the curves would be straight lines through the origin n_2 being always proportional to n_1+n_2, but with the Marconi valve only the first portions of the curves are straight lines. With the grid at 20 volts and the plate at 4 volts, the plate current n_2 is only proportional to the total emission n_1+n_2 when it is less than 1·6 milliamps. With the plate at 8 volts the proportionality holds till the plate current is 3 milliamps., while 5 milliamps. is the limit when the plate is at 12 volts. Figs. 2 and 3 show similar results,

Fig. 2.

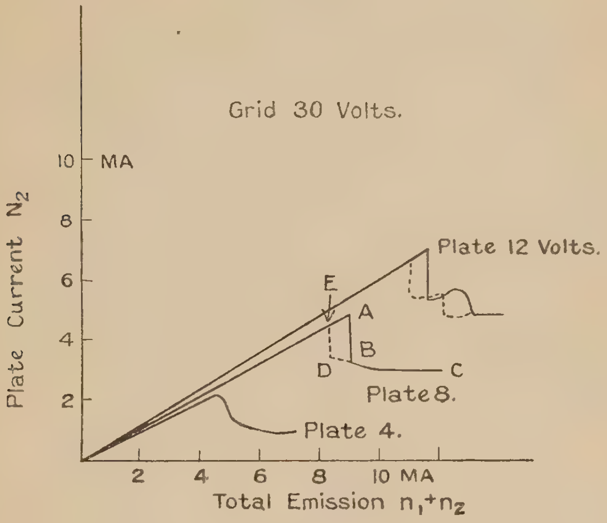
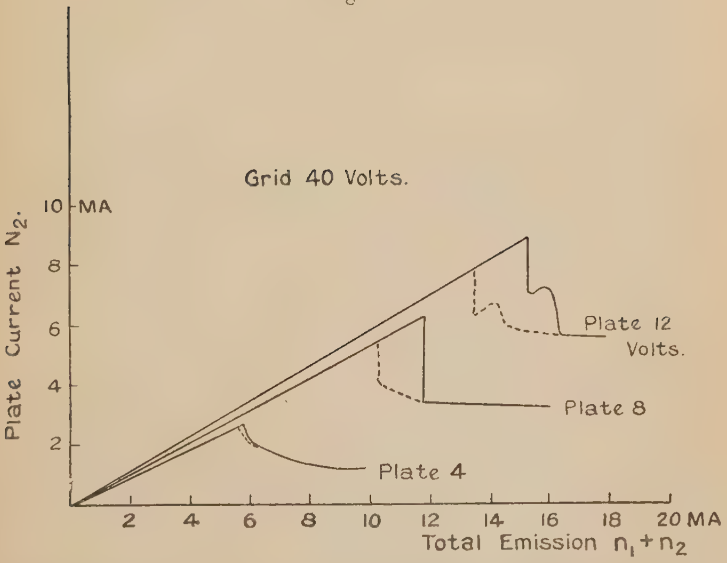


Fig. 3.



and indicate that the range of values of n_2 over which it is proportional to n_1+n_2 is increased if either the grid potential or the plate potential be increased.

If the total emission n_1+n_2 be increased beyond the range over which n_2 is proportional to n_1+n_2 in all cases the plate current n_2 decreases. If the plate and grid potentials are comparatively small, as in fig. 1, the decrease of n_2 with increasing n_1+n_2 is gradual, but for the higher values of grid and plate potential, as in some of the curves in figs. 2, 3, the fall is abrupt. For example in fig. 3, when the grid is at 40 volts and the plate at 8 volts, the largest plate current obtained is 6·4 milliamps. when the total emission is 11·7 milliamps. The slightest increase in the filament temperature causes the plate current to drop to 3·4 milliamps. for almost exactly the same total emission. The grid current of course rises abruptly by an equal amount.

If the total emission is further increased beyond the point where the drop in the plate current occurs the plate current remains low, though in one or two of the curves a small second maximum plate current is obtained for very high emissions.

The straight portions of the curves can be taken as giving a measure of the proportion of the electrons leaving the filament which pass through the grid, and therefore after the drop in the plate current occurs a large number of electrons which pass through the grid must fail to reach the plate and must return to the grid. An example will perhaps make this clearer. In the case in which the grid is at 40 and the plate at 8, the maximum plate current is 6·4 m.a., the filament emission being 11·7 m.a., that is $\frac{64}{117}$ of the electrons from the filament pass through the grid, the remainder being collected on the grid.

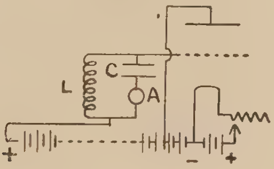
When the emission is 14 m.a. the current passing through the grid is therefore 7·7 m.a., but the curve shows that the plate current for this emission is only 3·3 m.a., and therefore more than half the electrons which passed through the grid must have been stopped before reaching the plate and have then returned to the grid.

There is one further important peculiarity of the curves to be mentioned, of which the curve for plate at 8 volts in fig. 2 is an example. In this curve if the emission is gradually raised the current increases up to point A, the sudden drop occurs to B, and further increase in emission takes it to C. If at this stage the emission is gradually reduced the curve will be retraced from C to B; at B, however, there is not an abrupt rise to A, but the curve from B to D is obtained, and the abrupt rise then occurs to E, after which the original curve is retraced. The curves for decreasing emission are all shown dotted where they deviate from the curves for increasing emission. It appears, therefore, that for certain values of the emission there may be two possible distributions of current in the valve.

The experimental facts therefore to be explained in the theory which will be given in section 4 are that if various currents from a source at zero potential are passed through a grid at potential V, the plate at potential V_0 (less than V), will receive the whole of this current if it is not larger than a certain critical value; only a proportion if it is above this value; while just below this critical value the plate can receive either the whole or only a proportion. The critical value depends on both V_0 and V.

3. A valve of this type can be used as a generator of continuous oscillations of either high or low frequency. It is only necessary to insert in the lead to the grid an oscillatory circuit as shown in fig. 4.

Fig. 4.



L is an inductance, C a capacity, and A a hot-wire milliammeter. If with the grid at, say, 40 volts and the plate at 8 volts the filament is gradually heated up, at the moment when the plate current experiences its sudden drop, oscillations will commence and be maintained in the oscillatory circuit, their presence being revealed by the hot-wire ammeter A. A similar result can be obtained for low frequency oscillations by inserting a telephone in place of the oscillatory circuit. The same heating of filament which caused high frequency oscillations will cause the telephone to emit a continuous hum showing that low frequency oscillations are being obtained.

The maintenance of these oscillations is independent of any electromagnetic or capacity coupling between the plate and grid. The method of maintenance can be seen from an inspection of figs. 2 and 3. If the plate is kept at 8 volts and the filament heated till the total emission is 9 milliamps., then if the grid potential is 30 volts, the plate current is 3·3 m.a., and the grid current is 9−3·3=5·7 m.a.

If the grid potential is increased to 40 volts the plate current is 5 m.a., and the grid current is therefore 4 m.a. Thus increasing the grid potential from 30 to 40 volts reduces the grid current from 5·7 to 4 m.a. A decrease of current for an increase of potential is an unstable condition—what is called a "negative resistance"—and in this state the valve is capable of maintaining oscillations.

Even if there are no oscillatory circuits in the leads it seems likely that short wave oscillations may arise in them or in the circuits of the milliammeters used for measuring the currents. The small kinks in the curves for the larger currents are probably due to this cause; the readings of the milliammeters in these regions being somewhat unsteady, as often occurs when intermittent oscillations are taking place.

4. The explanation of the preceding results is evidently to be looked for in the fact that the field between the electrodes is determined not only by the potentials of the electrodes, but also by the charge on the electrons which happen at any instant to be in the space between the electrodes. For simplicity the electrodes may be taken as parallel plates a distance d apart, kept at potentials V_0 and V_1. The distance x is measured from the plane which is at the potential V_0.

Let the current i per sq. cm. flow between the planes carried by electrons which started from a filament at zero potential. At the point x let V be the potential, v the velocity of the electrons, e their charge, m their mass, and let ρ be the charge per c.c. at x. The current is evidently independent of x, but V, v, and ρ are functions of x.

Then the general equations are :—

$$\left.\begin{aligned} \tfrac{1}{2}mv^2 &= eV \\ i &= \rho v \\ \frac{d^2V}{dx^2} &= 4\pi\rho \end{aligned}\right\} \text{(A).}$$

Apparently no general solution of these equations has been published, but a special case was solved by Child *. He found that if $V_0=0$, *i. e.*, if the electrons start with zero velocity at one electrode, then the maximum current the other electrode could receive per cm. was proportional to $V^{3/2}/d^2$ and that the corresponding potential distribution between the plates was $V=V_1\left(\frac{x}{d}\right)^{4/3}$.

The reason this is the maximum possible current is that the corresponding distribution causes the electric force to be zero at the plane from which the electrons start.

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* Phys. Rev. 1911, p. 499.

If the supply of electrons is insufficient to maintain this maximum current then a smaller current will flow. The field due to the charged electrodes will still be distorted, but not to so great an extent.

The above results were extended by Langmuir * to cases of cylindrical electrodes and electrodes of any shape. He found the current was still proportional to the three-halves power of the potential difference.

If, instead of the electrons leaving the zero-potential plane and being accelerated up to the plane of potential V_1, which they reach with a velocity $\sqrt{\frac{2e}{m}V_1}$, we start them back from this plane with this velocity and let them run in the retarding field to the plate, the equations (A) are unaffected, i and v having changed sign; the boundary conditions are also the same, and therefore the maximum current which can just get across is the same as before, and the resulting potential distribution is the same.

The case we are dealing with is rather more complicated than this. Let the plane at potential V_0 represent the plate and that at V_1 the grid, the filament being taken as zero. The electrons from the filament have the velocity $\sqrt{\frac{2e}{m}V_1}$ as they pass the grid, and they move in a retarding field up to the plate, but in all the experiments done V_0 was not zero but positive.

The boundary condition upon which the previous results were based, that in the limiting case the electric force just outside the electrode is zero, no longer holds, for the electrons hit the plate with a velocity $\sqrt{\frac{2e}{m}V_0}$, and will therefore reach it whatever the force at the plate. We must look elsewhere for a force which can limit the current reaching the plate.

The general equations have not been solved for this particular boundary condition, but it is easy to see what happens without attempting a solution. In fig. 5 let OA be equal to V_0, GB equal V_1, and OG be the distance between the plate and grid, then the ordinates of the straight line AB represent the potentials at the various points between the plate and grid when no current is flowing.

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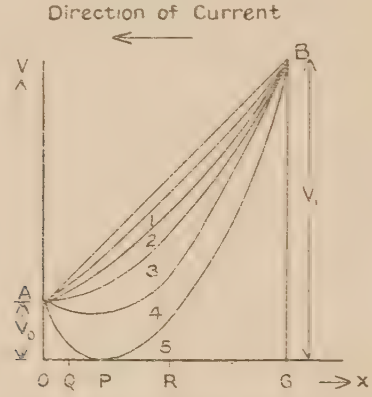
* Phys. Rev. 1913, p. 450.

Now suppose a small current passes the grid and flows to the plate, the electrons having velocity $\sqrt{\frac{2e}{m}V}$ at a place whose potential is V. The passage of this current affects the potential distribution, which becomes something like curve 1. If the current is increased the distortion of the field is more and we get curve 2, a larger current still will give 3, and so on with 4 and 5.

Fig. 5.



Distribution of Potential between plate at O and grid at A.

Curve 3 is drawn as that one of the family which is parallel to Ox at the plate, that is the electric force is zero at the plate. In curve 4 we get a reversal of the electric force between the electrodes, the electrons reach a minimum velocity at the place where the tangent is parallel to Ox, and then accelerate again till they reach the plate. Curve 5 is the limiting one. At P the electrons come momentarily to rest, the potential being zero and the force also zero, and then move on to the plate.

Curve 5 represents a state of affairs to which we can apply Child's results. If i is the current from grid to plate, then i satisfies the boundary conditions for maximum current between parallel planes distant apart OP charged to potentials V_0 and 0, and also for parallel planes distant apart PG charged to potentials V_1 and 0.

Hence $i = \frac{kV_0^{3/2}}{OP^2} = \frac{kV_1^{3/2}}{PG^2}$, k being a constant, from which both i and the position of P can be found in terms of V_0, V_1, and the distance between grid and plate.

The potential distributions can also be calculated :—

To the right of P $\quad V=V_1\left(\frac{x-\text{OP}}{\text{PG}}\right)^{4/3}.$

To the left of P $\quad V=V_0\left(\frac{\text{OP}-x}{\text{OP}}\right)^{4}.$

In all the curves 2 to 5 all the electrons passing the grid reach the plate, and the calculations just made determine the maximum current the plate can receive under these conditions. The question which next arises is, What happens if we force through the grid a current larger than this maximum? In the first place it is evident that the curve cannot sink below the x axis, for all the electrons would be brought to rest at the point nearest to G where the curve cuts the axis, and the force there would tend to send them back to the grid, none would reach the plate, and hence there would be no space-charge between this point and the plate, and the assumed distribution is therefore impossible.

The remaining possibilities are distribution curves which touch Ox at points other than P. We can at once rule out the possibility of such points being nearer to O than P, for if P were the point of contact of one of the curves the plate current would be $\frac{kV_0^{3/2}}{\text{OQ}^2}$, and the current passing the grid would be $\frac{kV_1^{3/2}}{\text{GQ}^2}$, but $\frac{V_0^{3/2}}{V_1^{3/2}}=\frac{\text{OP}^2}{\text{PG}^2}$, and therefore the plate current would be larger than the current entering through the grid, which is impossible. We are reduced therefore to potential curves which touch Ox at points such as R to the right of of P. A calculation similar to that just made would show that to make $V=0$ at R, and also the force $\frac{dV}{dx}$ zero there, would require a larger current from the grid than the plate receives; this means that some of the electrons which come to rest at R must return to the grid, and therefore to the right of R we are dealing with space-charges due to both direct and return currents. It is necessary then to examine how equations (A) would be modified in such a case.

Let i be the current passing through the grid from the filament side, i_1 the current returning from R towards the grid. The balance $i-i_1$ goes on to the plate. Let ρ be the charge per c.c. at distance x due to current i and ρ_1 that due to current i_1.

Then the velocities of the electrons, whether coming or returning, is the same at the distance x, being given by

$$\left.\begin{array}{ll} & \tfrac{1}{2}mv^2 = e\mathrm{V} \\ \text{also} & i + i_1 = (\rho + \rho_1)v \\ \text{and} & \dfrac{d^2\mathrm{V}}{dx^2} = 4\pi(\rho + \rho_1) \end{array}\right\} \text{(B)}.$$

These equations give exactly the same solution as (A) if $i + i_1$ replaces i, and we thus find that the current to the right of R is given by

$$i + i_1 = \frac{k\mathrm{V}_1^{3/2}}{\mathrm{RG}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The current to the left of R is the current i_{P} reaching the plate :—

$$i_{\mathrm{P}} = i - i_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and
$$i_{\mathrm{P}} = \frac{k\mathrm{V}_0^{3/2}}{\mathrm{OR}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From which i_{P} can be found in terms of i for given values of V_1 and V_0. It should be noted that the necessary condition that the stream of electrons entering through the grid should divide into two streams, one going on to the plate and the other returning to the grid, is that at some point both $\mathrm{V}=0$ and $\dfrac{d\mathrm{V}}{dx}=0$. For it is necessary that the electrons should come to rest, and in addition it is also necessary that at the place where they come to rest the electric force should be zero, as otherwise the stream would not divide there, since they would all start again in the direction of the force. Thus all the possible potential distributions for cases where all the incident electrons do not reach the plate must touch Ox somewhere between P and G.

The solution of equations 1, 2, 3 giving i_{P} in terms of i is a tedious business, and all the information required can be got more easily by working out the currents for different values of OR as below.

Take the special case grid at 40 volts and plate at 8 volts above the filament, the distance from plate to grid being 1 cm.

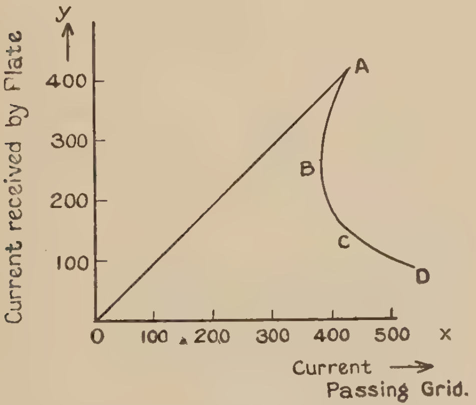
The maximum current which can reach the plate causes the potential to drop to zero at a distance OP$=\cdot 23$ cm. from the plate (calculated from $\dfrac{8^{3/2}}{\mathrm{OP}^2} = \dfrac{40^{3/2}}{(1-\mathrm{OP})^2}$), and the magnitude of this current in arbitrary units is 426. Any current less than this can flow from the grid to the plate causing some such potential distribution as 1, 2, 3, or 4.

The currents for potential distributions which touch Ox at R where OR is greater than ·23 are shown in the table following, i being the current entering through the grid and i_P the current reaching the plate.

OR.	i.	i_P.
·24	416	392
·25	406	360
·26	396	333
·27	391	309
·3	383	250
·35	393	178
·4	421	141
·45	466	112
·5	548	91

These results are shown graphically in fig. 6, the current entering through the grid being plotted along Ox, and the number reaching the plate along Oy. The straight part of the curve corresponds to the currents which cross without any current returning to the grid, and the remainder of the curve comes from the table.

Fig. 6.



It is seen that currents up to about 380 coming through the grid go direct across to the plate; but for currents between 380 and 426 there is the rather unexpected result that there are three possibilities. As an example, if a current of 400 units is forced through the grid either (1) all the 400 units reach the plate, (2) 350 reach the plate and 50 return to the grid, or (3) 170 reach the plate and 230 return to the grid.

For currents larger than 426 there is only one possible plate current which decreases as the current forced through the grid increases.

If a similar calculation is performed when the plate is at 12 volts, the curve obtained is similar, but the straight portion is longer, the maximum plate current being larger than when the plate is at 8 volts.

5. It is easily seen that the method of conducting the experiments described can obtain from fig. 6 a curve like those actually obtained. The current passing through the grid from the filament is very fairly accurately proportional to the total current leaving the filament, and therefore, by an alteration of scale, fig. 6 will show plate current plotted against total emission. As the filament temperature is increased we move along OA, and will reach A unless the condition represented by the curve ABC is more stable than the last part of the straight line OA. At A a further increase of grid current can only take us to the portion CD, and there is therefore a sudden drop from A to C, after which the plate current decreases as the current from the grid increases.

When the return journey is made, decreasing the heating emission brings us a long DCB unless the state C to B is so unstable that the currents charge to distributions given by the curve BA or OA. At B a further decrease of emission gives no alternative except to return to OA, and a rapid rise occurs at B. The experiments show that OA is stable when traversed by gradually increasing the filament emission and CB is stable when traversed by retracing it. It is of interest that if we are near A on the portion OA and the batteries charging the plate or grid are momentarily disconnected and replaced the plate current sinks to the value given by the curve CB. The only method of getting from O to A is to keep the grid and plate batteries attached and increase the filament heating.

So far, except in one or two doubtful cases, it has not been possible to get the currents in a distribution corresponding to the portion BA of the curve.

6. There is thus a very fair agreement between the experimental and calculated curves, and what differences there are can be accounted for by the assumptions made in the theory.

The main differences are that the grid and plate were taken as parallel planes instead of coaxial cylinders, and the filament as an equipotential, whereas, in fact, there is down it the voltage drop of about 4 volts, due to the heating current. The theory also accounts for the fact that the maximum current which can reach the plate will be increased if either the plate potential or the grid potential is increased.

The reason for the non-occurence of the chief phenomena with the Mullard valve is that owing to the dimensions the maximum current which can pass to the plate for a certain potential of the grid (and any plate potential) is greater than the maximum current which can flow from the filament for that particular grid potential. It is therefore impossible to force through the grid more current than the grid-plate space can carry to the plate. The maximum current which can flow to the plate gets less as the distance between the grid and plate is increased, and if the plate diameter is about 3 times the diameter of the grid it becomes possible to pass through the grid more current than the space can carry, and the drop in the plate current will occur.

7. An interesting point arises with regard to secondary emission of electrons from the plate due to the impact of the primary ones. For any value of the current passing the grid greater than that which causes the potential distribution 3 in fig. 5, the force at the plate tends to take electrons back to it, and therefore for all these currents the usual effects due to secondary emission will be absent (unless there is an appreciable velocity of emission).

Another suggestive question is whether a potential distribution curve could touch the axis Ox at more than one point.

If there are only electrons present this is not possible, but if, in addition, there are positive ions present it could theoretically occur. The electrons would come momentarily to rest at the points where the curve touched the axis Ox, at which points the positives would have their maximum velocity while they would have their minimum velocity at intermediate positions where the electrons were moving fastest. It is probable that some such condition exists in the striated positive column.

I have to thank Professor Townsend very much for advice and criticism.

C. *The Absorption of Ultra-violet Light in Dilute Solutions.* *By* C. J. Webber Grieveson, *B.A.*, *B.Sc.*, *Formerly Demy of Magdalen College, Oxford* *.

Introduction.

1. In his paper on the absorption of ultra-violet light in solutions (Phil. Mag. xvii. p. 710, May 1909), Dr. F. B. Pidduck gives an account of some experiments with solutions of common salt and potassium bromide in distilled water and with tap-water. According to his results about 1·5 parts of potassium bromide per million reduce the transparency of 15 mm. of distilled water by 25 per cent. If substances can be found which absorb very strongly in dilute solution, *e. g.*, about ten times as strongly as potassium bromide, it may be possible to use this absorption to measure very weak concentrations of these substances. It has been suggested that if a substance of this sort could be obtained, then in certain cases the volume-rate of flow of a river might be found by adding a quantity of the substance to the water at a certain place and noting the change of concentration further down. It was with the object of obtaining some information on this matter that the investigation summarized below was undertaken.

Apparatus and Method.

2. In general construction the apparatus follows the usual parallel plate form, arranged so that the U.V. light can fall on one of the plates, absorption being measured by the change in the photo-electric effect. But in order to compare absorptions more directly, this plate is divided into two equal parts, and to reach these parts the U.V. light has to pass through one or other of the quartz-bottomed vessels containing the liquids. The two plates—*i. e.* the two parts of the upper plate (P_1, P_2 in fig. 1)—are semi-circular, cut from one piece of brass and silver-plated. Each is mounted on two long ebonite pillars (not shown) and thus rigidly supported below the top plate (P) of the case. The common lower plate of the condenser consists of a silver-plated gauze (G) mounted on a stout metal ring supported by ebonite pillars. A suitable saturation potential difference between the plates is maintained by a battery of small accumulators. By using four brass pillars fitted with screw-heads instead of the usual

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* Communicated by Prof. J. S. Townsend, F.R.S.

three to support the top plate P, the latter can easily be turned through two right angles and the plates P_1, P_2 interchanged. The sides of the apparatus are screened by a cylindrical brass case hanging from the top plate. Fig. 1 illustrates the construction of the apparatus, although it is not strictly a central section of it. Examples of the supporting pillars and ebonites are introduced slightly out of their true position to show the method of mounting adopted.

Fig. 1.

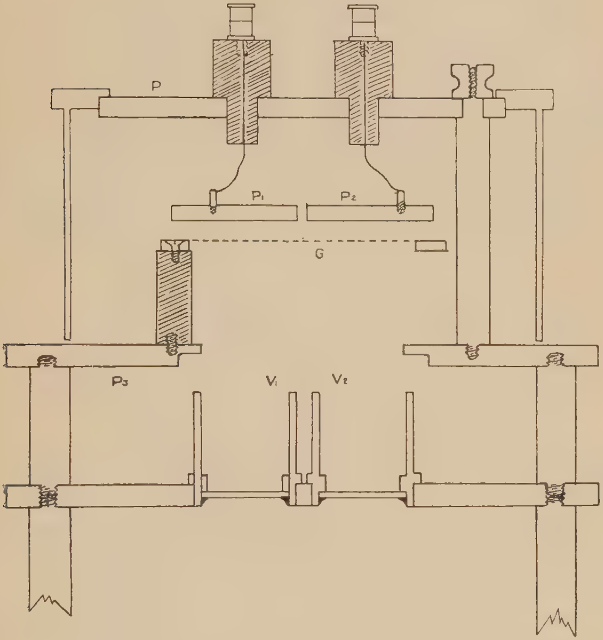


Diagram illustrating form of Plate Apparatus.

Dimensions.

Diameter of silver plates (P_1, P_2)	7·3 cm.
Distance of P_1 and P_2 below top plate P	2·5 cm.
Distance between P_1 and gauze G	0·7 cm.
Internal diameter of gauze-ring	6·4 cm.
Height of gauze G above plate P_3	2·8 cm.
Solution Vessels (V_1, V_2):	
Internal diameter	2·5 cm.
Overall height	3·1 cm.

Vessels centred at 3·1 cm. apart.

Over apertures near the centre of a stout brass plate some distance below the grating stand the two vessels V_1, V_2—cylindrical and with quartz bases—used to contain the solutions. The line joining their centres is perpendicular to the line of separation of the semicircular plates P_1, P_2, so that each vessel is directly under the middle of one of these plates. Ultra-violet light from a spark-gap parallel to the line of separation of the plates enters the vessels from below and passes up through the solutions to the plates above.

3. The photo-electric effect is measured by an electrometer and induction balance connected with the parallel plate apparatus by a special key (K, fig. 2). In parallel with the plates P_1, P_2 are the inner plates of two similar condensers C_1, C_2, whose outer plates may be raised to any desired potential by a battery connected through two potentiometers R_1, R_2 as shown in fig. 2; X is a small sliding rheostat used as a fine adjustment when necessary.

Fig. 2.

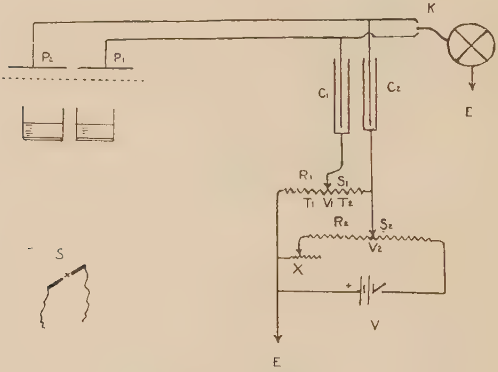


Diagram of Apparatus.

In performing the experiment the more transparent solution is put under the plate P_2, whose corresponding condenser C_2 is connected directly with the slider S_2 of the main potentiometer R_2. The spark is put on for a time and the electrometer is kept undeflected by adjusting S_2. Then K is switched over, connecting the electrometer with the other plate P_1. In general the electrometer is deflected, but if the ratio slider S_1 (on the potentiometer R_1) has been placed at the correct position to balance the charge on P_1, there is no movement. It follows from the theory of the system that if in this case q_1, q_2 are the charges acquired by the plates P_1, P_2, respectively, and if v_1, v_2 are the potentials of the sliders S_1, S_2, respectively, then

$$q_1 = c_1 v_1$$

$$\text{and} \qquad q_2 = c_2 v_2.$$

Also, if the resistances of the parts into which R_1 is divided by S_1 are r_1 and r_2, then

$$\frac{v_1}{v_2} = \frac{r_1}{(r_1 + r_2)}.$$

$$\text{Hence} \qquad \frac{q_1}{q_2} = \frac{c_1}{c_2} \cdot \frac{r_1}{(r_1 + r_2)}.$$

Replacing one of the solutions—the one under P_1—by a solution of another strength we get new values for q_1 and r_1 such that

$$\frac{q_1'}{q_2} = \frac{c_1}{c_2} \cdot \frac{r_1'}{(r_1 + r_2)}.$$

$$\text{and so} \qquad \frac{q_1'}{q_1} = \frac{r_1'}{r_1}.$$

Hence the position of the slider S_1 is a measure of the photo-electric effect and so of the transmitted light. It has been stated, however, by Griffith that the photo-electric effect (E) is not exactly proportional to the intensity (I) of the light but that E/I increases with I and at a gradually increasing rate. (For the reference see Pidduck's paper, *loc. cit.*) Subject to this proviso—which is disputed by other experimenters—the ratio $\frac{r_1'}{r_1}$ [for convenience referred to later as the transmission coefficient, μ] measures the relative transparency of the two liquids.

4. In general, the method of procedure was to take as the absorption standard a depth of 10 mm. of distilled water and to compare other liquids and depths with this. Before a specimen of a solution was examined both vessels were filled to a depth of 10 mm. with distilled water and the value r_1 of the ratio resistance was determined for no deflexion. The water in one of the vessels was then replaced by the same volume of the solution and the new value r_1' found. The water in the second vessel remained unchanged and formed a definite standard of comparison by which were eliminated errors arising from variations in the timing and the brilliance of the spark. To test this compensation the spark was purposely altered in length and intensity, and over a wide

range the consequent change in the reading was less than the general experimental error. In the experiments on the solutions care was taken to keep the spark working as steadily as possible.

Other errors liable to arise are those due to lack of uniformity of the solutions. These were very carefully made up and were kept in closely stoppered bottles. Even then one or two substances showed irregularity, the solutions tending to become more opaque with dilution. This was afterwards found to be due to traces of impurity. Substances which showed this effect invariably gave uncertain readings near these critical strengths. In the results recorded below only those substances are mentioned whose solutions gave readings that could be determined definitely.

To ensure constant electric conditions during measurement the spark was kept on just long enough for the slider to reach the same potentiometer division every time a reading was taken.

Solutions Tested and Results Obtained.

5. Among the substances examined was a series of some of the salts of sodium in order to compare the effects of the acid radicle on the absorption. Tap-water also was tested and the effect of adding a certain proportion of tap-water to distilled water solutions. Graphs of the change of the transmission coefficient (μ) of these solutions with concentration have been prepared, and it is by these curves that the results are most easily studied. In general form they are all similar (see fig. 3). Starting from the vertical axis at $\mu=1$ they fall more or less steeply at first but at a gradually decreasing rate until the gradient becomes very small and they approximate to straight lines slowly approaching the horizontal axis.

6. The chief results are as follows :—

Curve 1. *Sodium Chloride.* (Fig. 3.)

The curve for sodium chloride is quite even and regular. It falls steeply at first, but gradually the slope decreases until for strengths above $2{\cdot}5 \,.\, 10^{-3}$ N it reaches a practically constant value. Different specimens agreed within $\frac{1}{2}$ per cent.

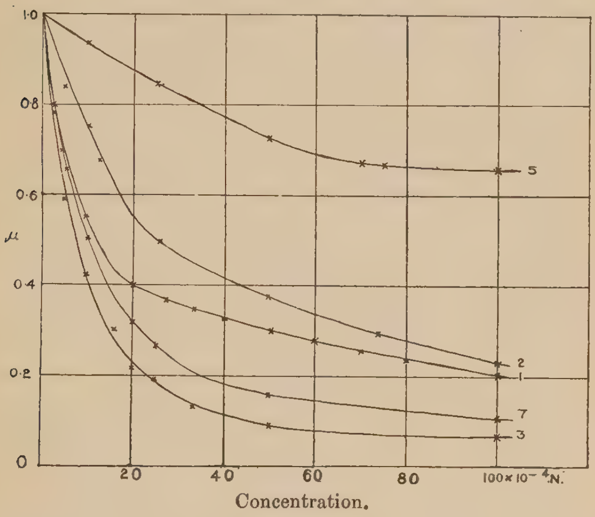
Curve 2. *Sodium Bicarbonate.* (Fig. 3.)

This curve does not fall quite as steeply as that for the chloride but it exhibits the same general form.

Curve 3. *Sodium Carbonate.* (Fig. 3.)

The normal carbonate absorbs much more readily in dilute solution than either the chloride or bicarbonate. The value of μ reaches 0·5 at a strength of about $6{\cdot}5 \,.\, 10^{-4}$ N (*i.e.* about 0·035 gm. per litre). For this absorption the chloride requires $1{\cdot}2 \,.\, 10^{-3}$ N (about 0·6 gm. per litre) and the bicarbonate $2{\cdot}6 \,.\, 10^{-3}$ N (about 0·22 gm. per litre). At the higher strengths the curve for the carbonate is noticeably flatter than the other two, so that concentrating beyond $5 \,.\, 10^{-3}$ N has comparatively little effect.

Fig. 3.—Substances in Table I.



Curve 4. *Sodium Diphosphate.* (Fig. 4.)

This curve falls even more steeply than curve 3 and it falls much lower before flattening out. The presence of 0·04 gm. per litre (about $2{\cdot}3 \,.\, 10^{-4}$ N) reduces μ to 0·5, and the presence of 0·3 gm. per litre reduces it to 0·02.

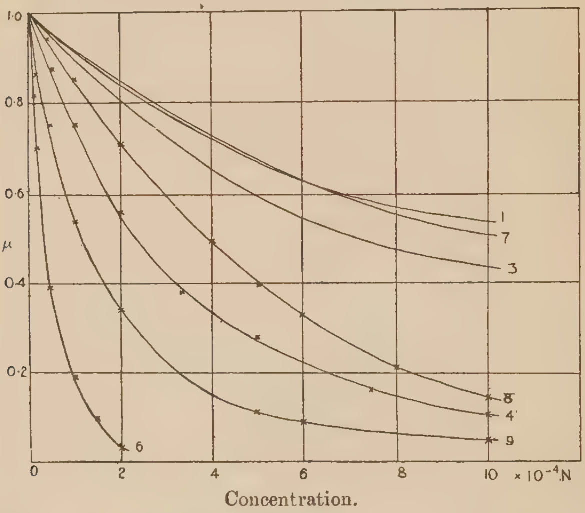
Curve 5. *Sodium Sulphate.* (Fig. 3.)

Sodium sulphate solution is remarkably transparent to the light from a zinc spark-gap. Even a centinormal solution does not reduce the photo-electric effect by one half, and further concentration would appear to have little effect for at 10^{-2} N the curve is almost horizontal.

Curve 6. *Sodium Nitrate.* (Figs. 4 & 5.)

As an absorber sodium nitrate is the most efficient of all the sodium salts examined. A concentration of $4 . 10^{-5}$ N absorbs half the effective light, and 10 mm. of a solution of strength $20 . 10^{-5}$ N is nearly opaque. This remarkably rapid fall in the curve was found with all the nitrates examined. In spite of the low concentration (from 1 to 10 parts per million) the individual readings all lie closely to the curve; the greatest divergence from the mean at any strength was not more than ½ per cent. In fig. 5 this curve is shown dotted.

Fig. 4.—Substances in Table II.



Curve 7. *Manganese Chloride.* (Fig. 3.)

At some of the lower concentrations solutions of this substance gave somewhat uncertain readings at first. The curve reaches $\mu = 0{\cdot}5$ at a strength of about 10^{-3} N.

As the curves for sodium chloride and carbonate and for manganese chloride (curves 1, 7, 3) overlap rather closely at the higher end in fig. 3 they are shown enlarged in fig. 4, which is on a larger scale.

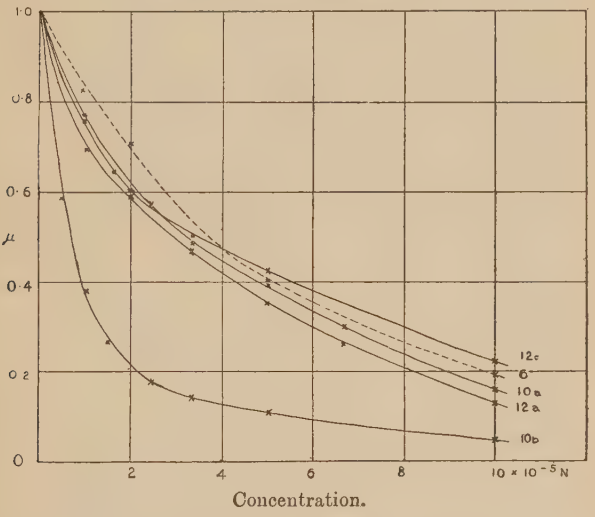
Curve 8. *Copper Sulphate.* (Fig. 4.)

Of the salts of copper so far examined the sulphate gives the most consistent results. The nitrate absorbs much more strongly, but it is less certain in its action. The curve for the sulphate falls quite steadily, passing $\mu = 0{\cdot}5$ at a strength of about $3{\cdot}5 \, . \, 10^{-4}$ N (*i. e.* about 0·03 gm. [anhydrous] per litre) and reaching $\mu = 0{\cdot}14$ at 10^{-3} N.

Curve 9. *Potassium Permanganate.* (Fig. 4.)

Potassium permanganate solutions absorb readily. A strength of 10^{-4} N is sufficient to reduce μ by nearly one-half and 10^{-3} N brings it down to one-twentieth. The very weak solutions (below 3 parts per million) showed a slight tendency to become more transparent on exposure to the air. The values given in Table II. are those found for the specimens as soon as they were put into the apparatus.

Fig. 5.—Nitrates (Table III.).



Curve 10. *Calcium Nitrate.* (Fig. 5.)

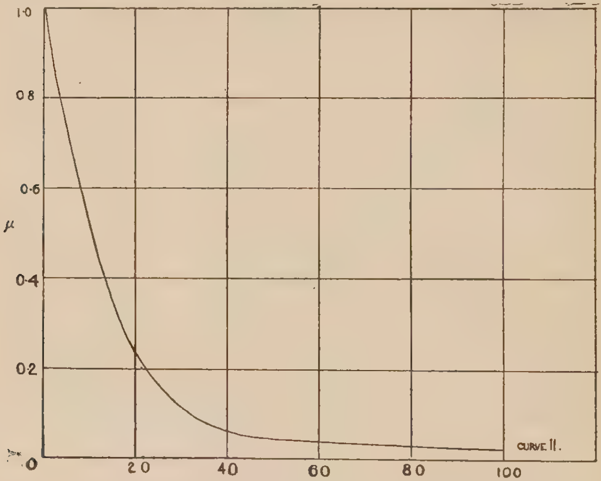
This like the other nitrates was found to absorb strongly. A solution stronger than $2 \, . \, 10^{-4}$ N is nearly opaque. The readings given by the individual specimens agreed well among themselves and gave mean values lying very closely to the curve.

The effect of increasing the thickness of the solution to 20 mm. is illustrated in the position of curve 10 *b*, which compares the absorption of 20 mm. of calcium nitrate solution with that of 20 mm. of distilled water. As would be expected this curve falls considerably below curve 10 *a*—the curve for a depth of 10 mm.—and μ reaches 0·5 at a strength below 10^{-5} N and $\mu = 0{\cdot}1$ at about $5 . 10^{-5}$ N. The individual points lie accurately on the curve although it falls so steeply.

Curve 11. *Tap Water.* (Fig. 6.)

Early in the course of the experiments it was found that 10 mm. of Oxford tap-water was practically opaque to the U.V. light from the spark-gap. If, then, solutions in tap-water were to be examined it was evident that only mixtures of tap-water and distilled water could be used as solvents, or else the spark would have to be made much more powerful. As the latter alternative would upset the continuity of the experiments a curve for mixtures of tap-water (filtered) and distilled water was taken off and some solutions in one or two of these mixtures were examined. Later the spark was slightly intensified also.

Fig. 6.—Mixtures of tap-water and distilled water (Table IV.).



Percentage of tap-water in mixture.

As tap-water is a mixture of dilute solutions of various substances, it is to be expected that mixtures of tap-water and distilled water would give a series of points on a curve similar to those already obtained. The curve found falls remarkably steeply and reaches $\mu = 0{\cdot}5$ with only 10 per cent. of tap-water in the mixture. For a 50 per cent. mixture $\mu = 0{\cdot}04$. Since Oxford tap-water has only about 0·3 gm. of dissolved substance per litre, it is evident that small quantities of a few different substances in solution make a very opaque screen for ultra-violet light.

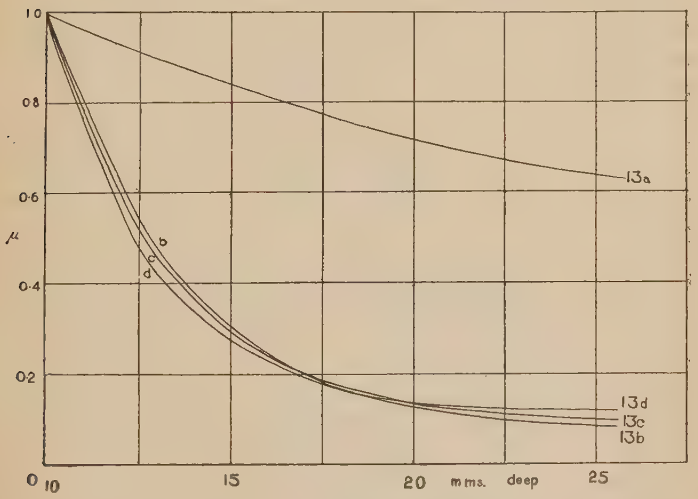
Curve 12. *Calcium Nitrate in Tap-Water Mixtures.* (Fig. 5.)

To examine to some extent the effect of the presence of other substances in the solution three separate series of readings were taken with solutions of calcium nitrate in mixtures of tap-water and distilled water. The mixtures used contained 10, 20, and 50 per cent. of tap-water respectively, and in each case the standard of comparison was 10 mm. depth of the mixture. In diluting these solutions it was arranged that the concentration of tap-water salts should remain constant throughout each series while the concentration of calcium nitrate was reduced.

All the curves obtained (curves 12 *a*, *b*, *c*) fall rather more steeply at first than the corresponding curve for solutions in distilled water (curve 10 *a*). The curves for the 10 and 20 per cent. mixtures are scarcely distinguishable at the weaker end, but increasing the proportion of tap-water to 50 per cent. of the dissolving mixture makes an appreciable difference. In fig. 5 curve 12 *b* is omitted for the sake of clearness.

Curves 13 *a*, *b*, *c*, *d*. *Effect of Thickness on Absorption.* (Fig. 7.)

Fig. 7.—Transmission and Depth (Table V.)



The last phenomenon to be examined was the change in the absorption due to increasing the depth of the solution. The absorption of 10 mm. of each liquid was taken as unity and with it were compared the absorptions of other depths.

Curves were drawn for distilled water (13 *a*), the 50 per cent. mixture of tap-water and distilled water (13 *b*), and solutions of calcium nitrate of strengths 10^{-5} N and $4 . 10^{-5}$ N in this 50 per cent. mixture (13 *c*, 13 *d*).

(a) *Distilled water.*

(b), (c), (d) *The* 50 *per cent. mixture and solutions in it.*

From the readings it is clear that the change of transmission with depth depends to some extent on the strength of the solution, although the general form of the curve remains the same. (The form of course varies to some extent with the particular solution.) It falls rapidly at first as the depth increases from 10 to 20 mm., but further increase in the depth produces comparatively little change. This, of course, agrees with the idea of selective absorption, and evidently a thickness of 20 or 30 mm. of tap-water would stop practically all the absorbable rays. The addition of small quantities of solute (in the particular case examined, calcium nitrate) to the tap-water, while reducing the actual transparency, made but little difference to the change of transparency with thickness. Each time the solution was strengthened the initial gradient became slightly steeper and at the same time the fraction absorbed in the last half centimetre was diminished. That is to say, in the stronger solutions more of the absorbable rays are stopped in the first centimetre and a proportionately smaller effect is produced by increasing the thickness.

From these curves it is evident that there is a depth beyond which it is of no advantage to go. In the case of the 50 per cent. mixture a thickness of 20 mm. absorbs much more than a thickness of 10 mm., but little is gained by increasing the depth beyond 20 mm. This maximum suitable depth depends on the strength of the solution. With a weaker solution than the equivalent of 50 per cent. tap-water it would naturally be greater than 20 mm. With a stronger solution it might be much less. As the strength of the solution decreases the bend in the curve becomes less pronounced and the initial gradient becomes less steep, so that the curve approaches that for distilled water (13 *a*).

Numerical Results.

7. The chief numerical results obtained in the course of the experiment are indicated in the following tables. In Tables I., II., and III. the first column indicates the concentration of the solutions in terms of 10^{-4} N or 10^{-5} N. The

other columns give the values obtained for the transmission coefficient, (μ), of these solutions at the various concentrations tested. In Tables I. and II. the value of μ is relative to the transmission of 10 mm. of distilled water.

In Table III. are grouped together the results obtained with solutions of calcium nitrate. The first column indicates the concentration in terms of 10^{-5} N. Columns 2 and 3 of the table give the values of the transmission coefficient for solutions in distilled water, column 2 being those for 10 mm. of solution relative to 10 mm. of distilled water, and column 3 those for 20 mm. of solution relative to 20 mm. of distilled water. The last three columns of Table III. show the values of μ obtained with solutions of calcium nitrate in mixtures of tap-water and distilled water. In column 4 the nitrate solutions were made up in a mixture of one of tap-water to nine of distilled water (known as the 10 per cent. mixture) and 10 mm. of this mixture was used as standard. In the dissolving mixtures used to obtain the figures in columns 5 and 6 the tap-water and distilled water were in the ratios 1 : 4 (the 20 per cent. mixture) and 1 : 1 (the 50 per cent. mixture) respectively. A depth of 10 mm. of the dissolving mixture was used as standard in each case, and the values of μ recorded are relative to the transmission of these standards.

Table IV. gives the values of μ obtained with mixtures of distilled water and tap-water (10 mm. deep), using 10 mm. of distilled water as the standard. Table V. illustrates the change in μ with change in depth of the solution. Four

TABLE I.

Transmission Coefficients of Solutions in Distilled Water. (*v.* Fig. 3.)

Concn. in 10^{-4} N.	Sodium Chloride. Curve 1.	Sodium Bicarbonate. Curve 2.	Sodium Carbonate. Curve 3.	Sodium Sulphate. Curve 5.	Manganese Chloride. Curve 7.
100	·202	·228	·068	·656	·101
50	·304	·375	·09	·727	·160
25	·383	·505	·194	·872	·265
10	·536	·765	·43	·945	·50
5	·670	·84	·591	—	·694
2·5	·801	—	·78	—	·81
0	1·0	1·0	1·0	1·0	1·0

examples are given: (i.) Distilled water; (ii.) A mixture of tap-water and distilled water in equal proportions (the 50 per cent. mixture); (iii.) & (iv.) Solutions of calcium nitrate of strengths 10^{-5} N and $4 \, . \, 10^{-5}$ N respectively in this 50 per cent. mixture.

In figs. 3 to 6 are given the curves corresponding with the tables.

TABLE II.

Transmission Coefficients of Solutions in Distilled Water. (*v.* Fig. 4.)

Concn. in 10^{-5} N.	Sodium Diphosphate. Curve 4.	Sodium Nitrate. Curve 6.	Copper Sulphate. Curve 8.	Potassium Permanganate. Curve 9.
100	·108	·018	·141	·052
50	·280	—	·398	·11
20	·571	·034	·71	·34
10	·756	·196	·874	·546
5	·871	·39	·95	·76
2	—	·701	·97	·87
0	1·0	1·0	1·0	1·0

TABLE III.

Transmission Coefficients of Calcium Nitrate Solutions. (*v.* Fig. 5.)

Concn. in 10^{-5} N.	In distilled water.		In the 10 per cent. mixture.	In the 20 per cent. mixture.	In the 50 per cent. mixture.
	Depth 10 mm. Curve 10 *a*.	Depth 20 mm. Curve 10 *b*.	Curve 12 *a*.	Curve 12 *b*.	Curve 12 *c*.
20	·040	—	·037	·04	·11
10	·16	·047	·133	·15	·22
5	·405	·105	·36	·3	·43
3·33	·48	·139	·483	·45	·505
2·5	·57	·179	—	—	—
2·0	—	—	·594	·59	·60
1	·77	·380*	·689	·76	·74
0	1·0	1·0	1·0	1·0	1·0

* At concentration $0·5 \, . \, 10^{-5}$ N, $\mu = ·589$.

Table IV.

Transmission Coefficients of Mixtures of Tap Water and Distilled Water. (*v.* Fig. 6.)

Percentage of Tap Water in the mixture.	Curve 11.
100 %	·021
50	·035
33·3	·089
20	·23
10	·504
5	·697
2	·85
0	1·0

Table V.

Change of Transmission Coefficient with Depth. (*v.* Fig. 7.)

Depth in mm.	Distilled Water. Curve 13 *a*.	50 per cent. mixture of tap-water and distilled water. Curve 13 *b*.	Solution 10^{-5} N of calcium nitrate in 50 per cent. mixture. Curve 13 *c*.	Solution 4.10^{-5}N of calcium nitrate in 50 per cent. mixture. Curve 13 *d*.
10	1·0	1·0	1·0	1·0
12·5	—	·547	·520	·478
15	·835	·304	·300	·277
20	·715	·124	·131	·135
25	·636	·085	·093	·117

In connexion with these results there is this to be said. The construction and dimensions of the apparatus naturally determine to a large extent the wave-lengths of the effective ultra-violet light. The light was not examined spectroscopically, but probably the wave-lengths present were chiefly the longer waves in the ultra-violet spectrum of zinc. A metal spark-gap in parallel with a condenser gives mainly the spectrum of the metal. Also, since in the actual apparatus the light had to pass through 10 cm. of air, 2 mm.

of quartz, 10 mm. of water or solution, and a further 6 cm. of air before reaching the silver plates, it is evident that only the longer waves could have got through to be effective. The fact that these wave-lengths occur in an absorption band of nitrate solutions determined the remarkable efficacy of the latter as absorbers.

Summary and Conclusion.

1. An apparatus is sketched and a method outlined by which the relation between the concentration of dilute solutions and their absorption of the ultra-violet light from a spark-gap may be studied.

2. Records are given of experiments with various substances in solution in distilled water, and curves are shown connecting the photo-electric effect of the transmitted light with the concentration. The effect of adding certain proportions of tap-water is also investigated.

It is shown that, in general, nitrates absorb more readily than some other substances, less than one part per million being sufficient to cause a measurable absorption in a depth of 10 mm. of solution. Of the other sodium salts examined, the phosphate and carbonate absorb fairly well, the chloride and bicarbonate require much stronger solutions to produce measurable effects, and the sulphate absorbs scarcely at all.

3. Finally, the relation between absorption and thickness of solution is examined in a few cases.

In conclusion, I should like to record my thanks to Professor Townsend, in whose laboratory the research was performed, for his kindly advice and encouragement during the course of the experiments.

CI. *Note on the Law of Force within the Atom. By* GEORGE GREEN, *D.Sc., Lecturer in Natural Philosophy in the University of Glasgow* [*].

X-RAY experimental investigation establishes very definite arrangements of atoms and atomic groups in crystalline and solid matter. According to modern ideas regarding matter, the mutual forces acting between atoms, which determine the equilibrium arrangements of atoms to form a crystal, are such as would arise when atoms act upon neighbouring atoms or electrons only in virtue of the forces depending on their electrical charges. By consideration of the conditions required for equilibrium of a homogeneous assemblage composed of positive and negative charges, it can, however, be shown that the inverse square law of attractive force between a positive charge and an electron cannot hold without modification when atomic distances between charges are reached. The inverse square law of attraction must give place to some law of repulsion between a positive and a negative charge, in order that the individual positive and negative charges may be able to retain the relative positions assigned to them in the experimentally determined space-lattice arrangement. Sir J. J. Thomson, in his recent papers [*] dealing with the subject of the electron theory of solids, assumes that the law of force between a positive charge e and an electron e is represented by

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[*] Communicated by the Author.

$$f=\frac{e^2}{r^2}-\frac{ce^2}{r^3}, \qquad \ldots\ldots \quad (1)$$

where c is a constant, and where the repulsive force ce^2/r^3 is supposed to come into operation only at atomic distances. No particular reason is stated in these papers for giving preference to the inverse cube law as the law of repulsive force just outside a positively-charged atom, although reference is made to the inverse cube law in an earlier paper [†]. The results arrived at by means of the law (1) given above prove that any indication of the correct form of the law of repulsion between a positive atom and an electron within atomic range would be of importance in establishing more satisfactorily the foundation of the electron theory of solids.

On the other hand, according to Bohr's theory of the atom, the inverse square law of attraction holds for the orbits of an electron within an atom, and also, according to α-ray experimental results obtained by Rutherford and others, the same law holds at distances within the innermost orbits of Bohr's theory.

The object of the present note is to indicate what seems to be a probable form of the law of force between a positive charge and an electron within atomic distances. With a law of force of the type under discussion below, it will appear that it is possible to harmonize the apparently opposite views referred to above, and in this way to obtain a link connecting two distinct fields of investigation.

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[*] Phil. Mag. xliii. p. 721; xliv. p. 657 (1922).

[†] Phil. Mag. xx. p. 239 (1910).

If we take ρ to represent a radius drawn from the centre of an atom, such that for all distances exceeding a small multiple of ρ the inverse square law of attraction holds, the law of force to be discussed below is of the type *

$$f=\frac{e^2}{r^2}\cos\frac{\rho}{r}; \quad \text{or} \quad f=\frac{e^2}{r^2}\cos\frac{\rho}{r}+\frac{ae^2}{r^n}\cos\frac{\rho}{r}+\frac{be^2}{r^n}\sin\frac{\rho}{r}. \quad (2)$$

Additional terms such as $e^{-\rho/r}$ may be included to represent a force ultimately falling to zero as r is diminished, but these do not immediately concern us. The particular case

$$f=\left(\frac{e^2}{r^2}+\frac{ae^2}{r^4}\right)\cos\frac{\rho}{r} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is worthy of study, even as as illustrative system only, f being positive for attraction and negative for repulsion.

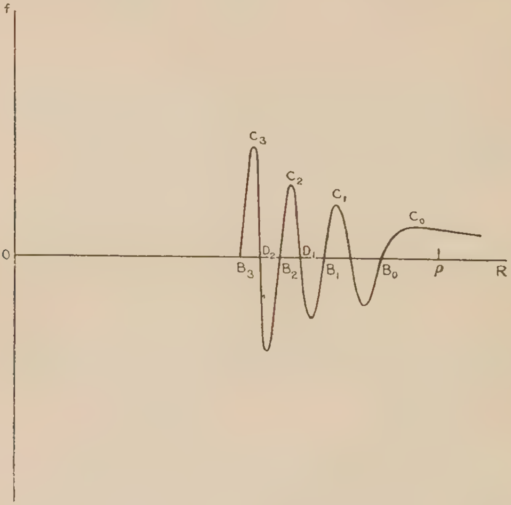

Diagram showing the force acting on an electron.

The force varies with r in the manner indicated in the diagram, where B_0, B_1, B_2, etc. represent positions within the atom at which an electron could remain at rest in stable equilibrium. These positions of equilibrium for an electron at rest correspond to values of r given by

$$\frac{\rho}{r_n}=(2n+\tfrac{1}{2})\pi\,; \quad n=0,\ 1,\ 2,\ 3,\ \text{etc.} \quad . \quad . \quad (4)$$

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* A similar law of force was discussed from quite a different standpoint by Sir J. J. Thomson in Phil. Mag. xxxvii. p. 419 (1919).

Similarly, maxima of the attractive force on an electron occur at the positions defined by

$$\frac{\rho}{r}=2n\pi,\quad n=1,\ 2,\ 3,\ 4,\ \text{etc.}, \quad . \quad . \quad . \quad . \qquad (5)$$

and represented by the points C_1, C_2, C_3, etc. in the diagram.

Consider now a slight radial displacement to be given to an electron initially at rest in one of the positions of equilibrium B_n. The restoring force corresponding to a displacement u is given by

$$F=\frac{e^2\rho}{r_n{}^4}\left(1+\frac{a}{r_n{}^2}\right)u. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

If m be the mass of an electron, the frequency ν of its vibration about the position B_n is accordingly given by

$$\nu^2\doteq\frac{e^2\pi^4}{m\rho^3}\left\{(2n+\tfrac{1}{2})^4+\frac{\nu}{\rho^2}(2n+\tfrac{1}{2})^6\pi^2\right\}, \quad . \quad . \qquad (7)$$

or, if a be an exceedingly small quantity, by

$$\nu=\frac{e\pi^2}{(m\rho^3)^{\frac{1}{2}}}\cdot(2n+\tfrac{1}{2})^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

The amount of work which must be expended in order to remove an electron from one of its equilibrium positions B_n to another B_p $(n>p)$ is represented by

$$\begin{aligned}W_n-W_p&=\frac{e^2}{\rho}\int_{r_n}^{r_p}\left(\frac{\rho}{r^2}+\frac{a\rho}{r^4}\right)\cos\frac{\rho}{r}\,dr\\&=\frac{ae^2\pi^2}{\rho^3}\left\{(2n+\tfrac{1}{2})^2-(2p+\tfrac{1}{2})^2\right\}, \quad . \qquad (9)\end{aligned}$$

an expression which is seen to depend only on the second term contained in the assumed law of force (3). The value of W_n alone, which represents the work required to remove an electron from position B_n to a position at rest at infinite distance, is

$$W_n=\frac{e^2}{\rho}+\frac{ae^2\pi^2}{\rho^3}(2n+\tfrac{1}{2})^2-\frac{2ae^2}{\rho^3}, \quad . \quad . \quad . \quad . \qquad (10)$$

and the corresponding expression for the position C_n at which the attractive force is a maximum is

$$W_n=\frac{2ae^2}{\rho^3}\,n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

The value of $W_n - W_p$ which we have obtained above represents also the amount of energy radiated corresponding to a change in the position of the electron from one equilibrium position to another. It is of interest to note that the expression is in harmony with a quantum theory, and the diagram on p. 1022 indicates clearly the manner in which energy would be radiated when an electron is in motion radially to or from the positive nucleus. If an electron originally at B_n receives just sufficient energy to allow it to reach the point D_n, it will then oscillate about the position B_{n+1}, and in so doing lose its energy gradually in waves which are of one definite frequency. If the electron were disturbed from B_n so as to reach D_n with a high inward velocity, it would then traverse a large range of r including many equilibrium positions before reaching the position at which it would ultimately settle after a series of diminishing oscillations. Taking the loss of energy by radiation proportional to the square of the acceleration at each instant, we see that the rate of loss would be very rapid so long as the inward radial motion continues. Each separate wave-length of the radiated energy would correspond with the movement of the electron from one of the equilibrium positions to the next—a distance which gradually diminishes as the inner positions are approached. The mean velocity of the electron between successive equilibrium positions likewise falls off during the inward motion, so that the energy radiation tends to be approximately of a uniform wave-length, as we may readily verify analytically. The frequency of the emitted radiation clearly depends on the initial energy of the inward motion, and this determines also the final position to which the electron would attain before coming to rest. We see therefore that the law of force under consideration provides a system in which energy would be radiated according to change of position of an electron within an atom in a manner in close conformity with the conditions of radiation loss postulated for a change of orbit of an electron on Bohr's theory of the atom.

So far we have retained the term ae^2/r^4 in the expression for the law of force; but in considering orbital motion of an electron round a positive nucleus, we can without loss limit the discussion to the simpler case where

$$f = \frac{e^2}{r^2} \cos \frac{\rho}{r} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This force is attractive within each range of r from

$$\frac{\rho}{r} = (2n + \tfrac{1}{2})\pi \quad \text{to} \quad \frac{\rho}{r} = (2n - \tfrac{1}{2})\pi ;$$

and accordingly it might appear to be possible for an electron to revolve steadily at any distance r_0 within the range with angular velocity ω, provided

$$m\omega^2 r_0 = \frac{e^2}{r_0{}^2}\cos\frac{\rho}{r_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

To test the stability of such an orbital motion, we may assume that the electron is disturbed slightly from its circular path by a radial force, so that in the subsequent motion the angular momentum of the electron remains constant. The equation representing the subsequent radial motion is

$$m(\ddot{r}-r\dot{\theta}^2) = -\frac{e^2}{r^2}\cos\frac{\rho}{r}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

When we take account of the condition of uniform angular momentum, replace r by r_0+z, and retain only the terms depending on the first power of z, the above equation becomes

$$\ddot{z}+\omega^2\left(1+\frac{2y^2}{\rho}\tan y\right)z = 0, \quad \text{where } y = \frac{\rho}{r_0}. \quad . \quad . \quad (15)$$

Hence a uniform orbital motion of the electron is stable, provided

$$\left(1+\frac{2y^2}{\rho}\tan y\right) > 0\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

that is, when $\tan y$ is positive, and also when $\tan y$ is negative but not greater than $\rho/2y^2$. Thus in each range of r from one of the equilibrium positions B_n to the neighbouring position of maximum force C_n, and to a small distance beyond C_n only, the assumed orbital motion is stable. An electron describing an orbit near any one of the positions defined by $\rho/r=2n\pi$, C_n, and subject to only a slight loss by radiation, would experience an exceedingly slow change of position towards B_n, because the loss of energy by radiation only affects the kinetic energy of the electron very slightly near C_n. In this neighbourhood the work done by the attraction of the positive charge upon an electron for any slight movement of the electron towards the nucleus has a maximum value; and this work energy has to be expended before the electron sensibly changes its position. Accordingly, it is clear that the orbital motions of an electron corresponding to any one of the positions indicated by C_n, C_{n+1}, etc., once established, would be nearly permanent, provided the natural radiation loss was small.

They would therefore resemble closely the electron orbits postulated by Bohr.

Consider now the values of the kinetic energy, angular momentum, etc., of an electron revolving about a nucleus in one of these orbits corresponding to the position $\rho/r_n=2n\pi$. In this orbit, with the usual notation, we have $m\omega^2 r_n=e^2/r_n^2$, and the kinetic energy of the electron is therefore $e^2/2r_n$ or $\frac{1}{2}m\omega^2 r_n^2$. Hence, in removing an electron from the orbit r_n to a position at rest at an infinite distance, an amount of energy T_n would be obtained, where $T_n=e^2/2r_n$. The loss of energy involved in a change of orbit of the electron from orbit r_n to r_p would be represented by

$$T_n-T_p=\frac{1}{2}\left(\frac{e^2}{r_n}-\frac{e^2}{r_p}\right), \quad . \quad . \quad . \quad . \quad (17)$$

or, since $r_n=\rho/2\pi n$, $r_p=\rho/2\pi p$, by

$$T_n-T_p=\frac{\pi e^2}{\rho}(n-p). \quad . \quad . \quad . \quad . \quad (18)$$

Similarly, the angular momentum of the electron in orbit r_n is easily shown to be given by A_n, where

$$A_n=(me^2 r_n)^{\frac{1}{2}}=\left(\frac{me^2\rho}{2\pi n}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (19)$$

and the change of angular momentum of the electron from orbit r_n to orbit r_p is accordingly

$$A_n-A_p=\left(\frac{me^2\rho}{2\pi}\right)^{\frac{1}{2}}\left\{\frac{1}{n^{\frac{1}{2}}}-\frac{1}{p^{\frac{1}{2}}}\right\}. \quad . \quad . \quad . \quad (20)$$

When we take n to represent some exceedingly large number, while the difference $n-p$ is small in comparison, the above expression for the change of angular momentum becomes

$$A_n-A_p=\left(\frac{me^2\rho}{8r_n^3}\right)^{\frac{1}{2}}.(n-p). \quad . \quad . \quad . \quad (21)$$

This form indicates that the change of angular momentum of an electron from each orbit to the next is sensibly uniform for a very large number of orbits on either side of orbit n.

Keeping n to represent some very large but definite number, let us now choose a succession of orbits corresponding to the positions C_n defined by the indices

$n, \frac{n}{4}, \frac{n}{9}, \frac{n}{16}, \frac{n}{25}$, etc. The energy of the electron corresponding to these orbits is proportional to the numbers $1, \frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{4^2}, \frac{1}{5^2}$, etc., respectively; the radii of these orbits are proportional to the numbers 1^2, 2^2, 3^2, 4^2, 5^2, etc., respectively; and the angular momenta are proportional to the numbers 1, 2, 3, 4, 5, etc., respectively. Hence these particular orbits can be identified with the system of orbits referred to in Bohr's theory of the atom. If we choose the constant n so that

$$2\pi \mathrm{A}_n = 2\pi \left(\frac{me^2\rho}{2\pi n}\right)^{\frac{1}{2}} = h, \quad . \quad . \quad . \quad . \quad (22)$$

where h is Planck's constant, the above system of orbits coincides with that of Bohr, and leads to the same value for the Rydberg constant, namely $2\pi^2 e^4 m/h^3$. The particular law of force now under discussion does not provide any reason why the group of orbits referred to in the preceding paragraph should be of more importance in the atom than the intermediate orbits. But it is clear that this can be secured by a proper summation of terms of the same type.

The properties of the atomic system which we have been discussing are also interesting in relation to the manner in which radiation would take place from such a system, which we have already referred to in connexion with change of position of an electron from one equilibrium position to another. Similar results regarding the frequency of energy radiated are obtained in the case of a change of orbit of the electron as in the former case. The peculiar feature of the orbital motion at any position C_n is that, while the motion is stable for exceedingly small disturbances, the range of stability is small especially for the inner orbits, as we see from equation (16) above. When a disturbance occurs sufficient to render $\tan y$ negative and greater than $\rho/2y^2$, the orbital motion becomes unstable. The electron would then begin to move outwards with at first a gradual increase in the radial velocity, and then a rapidly increasing radial velocity when the force acting on it becomes repulsive. According to the law (12), the kinetic energy acquired by the electron in any range of r for which the force is repulsive is exactly equal to the amount required to enable it to surmount the succeeding range in which the force is attractive, loss of energy by radiation being neglected.

Through loss of energy the outward movement of the electron might come to an end in one of the outer orbits, but with a moderately large initial disturbance the electron would escape from the positive nucleus altogether. In the case where a disturbed electron is retained in one of the outer orbits, the outward movement would be brought to an end suddenly through loss of energy, and the train of waves radiated would be practically of a uniform wave-length, as in the case already referred to on p. 1024 above. The same explanation applies to the case of an electron acquiring suddenly an increase of angular momentum. It must move outwards, with loss of energy by radiation in each successive range of positive or negative force, until it reaches an orbit corresponding to the angular momentum which it now possesses. The outward movement would begin suddenly and come to an end suddenly, and the mean frequency of the train of waves radiated would be completely determined by the initial and final orbits of the electron.

As already stated, with relatively small loss of energy by radiation an electron might readily escape from the nucleus, carrying with it the bulk of the energy belonging to the orbit from which it set out. The relation of such an action of expulsion of an electron to the photo-electric effect is obvious; and it is clear also from equation (16) above that light-waves capable of disturbing an electron so as to enable it to escape would require to have a frequency in close agreement with the natural frequency of disturbed orbital motion of the electron.

We see, then, that the law of force (2), which we have been discussing, gives us an atomic system whose essential features are in conformity with Bohr's theory of the atom and with quantum theory. It admits also of equilibrium positions for an electron within the atom. The above discussion may be useful in providing a physical picture of an atomic system whose properties are similar in many respects to those of the Bohr atom, and in indicating a form of the law of force between an atom and an electron when atomic distances are reached.

CII. *An Oscillograph Study of the Aluminium Valve.* *By* F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter**.

[Plate XI.]

1. *Introduction.*

When diluted sulphuric acid is electrolysed with an anode of aluminium, the anode becomes coated with a grey film, and the polarization observed seems to be partly galvanic and partly dielectric. According to W. A G. Schulze † the valve action of such an aluminium rectifier is due to the formation of a very thin layer of gas, of high resistance, and a thicker, porous layer of aluminium oxide, the pores of which are filled with electrolyte and gas. The whole may be compared with a condenser; since, however, the capacity and resistance of the formed anode are both very high, the charge accumulated cannot disappear in a moment. The resistance of the oxide layer appears to be very small in comparison with that of the gas layer, and the ohmic resistances are by no means constant.

F. Streintz and F. Fiala ‡, in experiments on gas generation from aluminium electrodes in diluted sulphuric acid, found that hardly any gas was liberated on open circuit; the electrolysis by 14 storage-cells gave very little oxygen at the anode, which collapsed in 24 hours. When the current was reversed before this collapse, the cathode—which had been the anode—gave the correct amount of hydrogen, and the relation between the current intensity in the anodic and cathodic directions, i_{12} and i_{21}, is

$$i_{12} = -\frac{a}{2} + \left[\left(\frac{a}{2}\right)^2 + b i_{21}\right]^{\frac{1}{2}},$$

where a and b are coefficients of practically equal value, and increase with the E.M.F. of the charging battery. The polarity

$$U = \frac{(i_{21} - i_{12})}{i_{21}}$$

increases with the charging potential V in such a way that UV becomes constant, starting from a certain value of V; that value of V is below 150 volts, but it cannot be fixed with any degree of accuracy. The value of U depends only upon the current density—increasing with the density—not upon V, provided that the density is not high. A valve effect was obtained by these experimenters only at high current density, and it depended upon the supply of anions per unit time.

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* Communicated by the Author.

† *Ann. d. Phys.* xxii. 3, p. 543 (1907).

‡ *Phys. Zeits.* xxii. p. 141 (1921).

Schulze * noted that during the formation of these electrolytic valves the P.D. rises first to the spark potential, then to the maximum potential, but sometimes there is a further slight rise. Both the porous film of the oxide and the effective oxygen film of high electrostatic capacity are exceedingly thin, especially the latter, and the film formation becomes more and more difficult as the temperature rises to 100° C. when more oxygen is liberated.

A. Smits † disagrees with Schulze's view that the passivity of aluminium during anodic polarization is due to the formation of a layer of alumina of high resistance. He considers that, although a coating of oxide or basic salt is formed at higher potentials, this explanation cannot be reconciled with the fact that at lower potentials, where passivity is also shown, the aluminium electrode remains bright, and that when the current is reversed the resistance disappears. Smits finds that, on anodic polarization, the potential of the metal becomes so strongly positive that the tension necessary for the separation of oxygen is reached with very low current densities. He considers that this change of potential is the primary phenomenon, and the separation of the oxygen, and subsequent oxide formation, is a secondary action. The increase of the aluminium potential is explained by the withdrawal of electrons from the metal being followed immediately by the aluminium going into solution. The formation of the aluminium ions within the solid metal proceeds with very slow velocity. Through the withdrawal of electrons and ions the metal surface passes into a state which resembles a metalloid, and it possesses an exceedingly small electrical conductivity. The aluminium surface, therefore, is a metal coating of great electrical resistance, and this coating is in turn surrounded by another of alumina.

The immediate destruction of anodic polarization on reversal of the current is explained by the fact that hydrogen, just as oxygen, though in a smaller degree, is a negative catalyst for the establishment of the internal metal equilibrium, but yet apparently acts positively catalytically when

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* *Ann. d. Phys.* lxv. 3, p. 223 (1921).

† *K. Akad. Amsterdam*, Proc. xxii. 9 & 10, p. 876 (1920).

it separates on a metal surface that has previously absorbed oxygen, since both negative catalysts then disappear with the formation of water.

This valve action of aluminium has been utilized by the author * in a modified form of the Wehnelt interrupter, in which the cathode is an aluminium plate and a platinum wire acts as the anode, these electrodes being immersed in a saturated solution of ammonium phosphate. In addition to possessing rectifying properties, this arrangement also acts as an interrupter. The present work is an investigation of the valve action of this interrupter under various conditions.

2. *Experiments.*

In the experiments described below, the wave-form of the current passing the valve was investigated by means of oscillograms. The oscillograph employed was a Duddell permanent magnet type having a vibrator specially stretched so that, if necessary, it was able to follow variations in the current up to 1000 alternations per second. The resulting curves were photographed by means of a falling-plate camera. The plate release in the dark slide was controlled by an electromagnet, and the plate could be adjusted, if desired, at different heights, so that the time-interval between the commencement of the current and the instant of photographing could be varied and measured by using a special rotating commutator. The vibrator—in series with a high non-inductive resistance—was placed in shunt with the main current.

The valve consisted of an aluminium plate, 8 sq. cm. in area, and a platinum wire, 0·12 sq. cm. surface area, both electrodes being immersed in a solution of ammonium phosphate. Alternating current of period 60 was used, and, accordingly, the anode was formed by one-half of the current cycle, the other half tending to neutralize such formation. In all cases the P.D. is the maximum value, and the current density is expressed in virtual amperes as read from a hot-wire ammeter.

A clear surface of the aluminium having been prepared and placed in the electrolyte, the form of the current was observed and photographed at different time-intervals after the current had commenced to flow in the valve. The oscillograms Nos. I., II., and III. (Pl. XI.) represent the current form after such intervals of 0·2 sec., 0·6 sec., and 0·8 sec. respectively. Rectification, which depended on the current density, was complete with 1·05 amps. per sq. cm. within 0·8 sec., the strength of the anode film in this short interval being such that it withstands the applied P. D. of 100 volts. The time-interval required for complete rectification increases as the current density falls, but complete rectification is never attained with very small current densities, even when the applied voltage is as low as 12 volts. Oscillograms Nos. IV., V., and VI. give the current forms with current density 0·4, 0·2, and 0·11 amp. per sq. cm., and applied P.D. 50, 24, and 13 volts respectively.

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* Proc. Roy. Soc. A, xcix. p. 324 (1921).

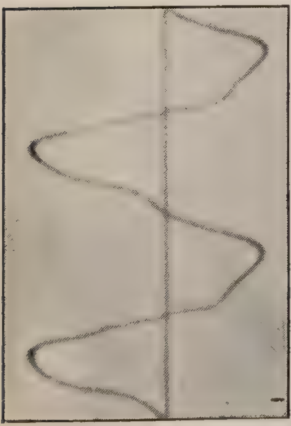
Contrary to previous statements, it was found that the temperature of the electrolyte did not affect the rectifying properties of the valve. This is illustrated by oscillogram No. VIII., in which rectification is practically complete, although the valve was placed in an oil-bath and maintained at 96° C. The current density in this case was 0·96 amp. per sq. cm. and the P.D. —100 volts.

After anode formation, if the aluminium were removed from the solution and dried, the anode was not active on replacing it in the electrolyte, and in order to restore its rectifying properties it was necessary to remove the oxide film and re-form the anode. This fact seems to indicate that the thin gas film, which according to Schulze is present, is removed when the anode is dried.

Impurities present in the electrolyte have a detrimental effect on the rectifying properties of the valve, and sodium chloride appears to be very prejudicial in this respect. Oscillogram No. VII. shows the effect of adding a trace of this salt; otherwise the conditions of the experiment were the same as those under which oscillogram No. VIII. was photographed. The chlorine ion appears to prevent the complete formation of the anode.

Self-induction in the circuit changes the form of the current curve and causes incomplete rectification. This is shown in oscillogram No. IX., in which the current density was 1·24 amps. per sq. cm., the P.D. 100 volts, and the self-inductance 20·5 henries.

The small time-interval necessary for the anode formation indicates that diffusion plays little or no part in the phenomenon. The film thickness must be very small, but, even so, the film is able to withstand a tension of 100 volts. A solid oxide film alone, without the existence of an oxygen layer, would be unlikely to maintain such a rectifying action. The fact that temperature has little effect on this valve action is important when the valve is used as an electrolytic interrupter. In the latter case considerable heat is developed; and if the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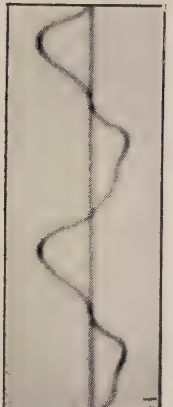
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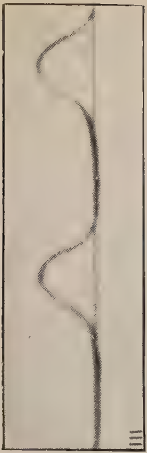
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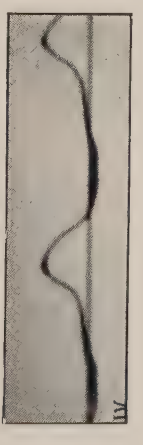
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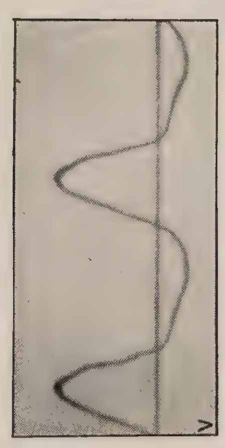
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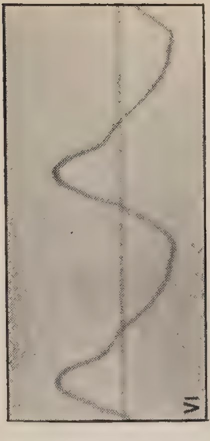
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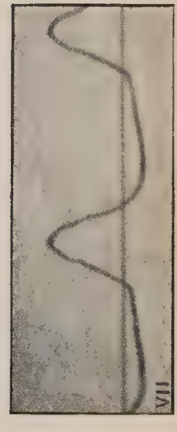
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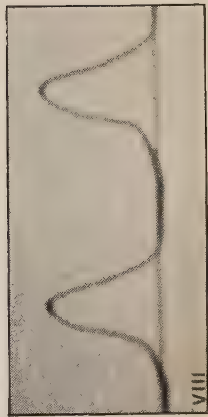
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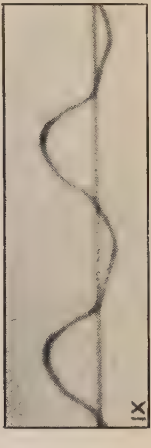
IX

Oscillograms of A.C. Period 60 rectified by the Aluminium Valve.

rectifying action ceased at high temperatures, this interrupter could not be employed with alternating currents, since in the event of such a cessation, the platinum wire, acting as the cathode during alternate half-cycles, would inevitably melt.

3. *Description of Plate.*

Oscillograms of A.C., period 60, rectified by the aluminium valve:—

I. Applied P.D. 100 volts. Current density 1·05 amps. per sq. cm. Current form, 0·2 sec. after current started.
II. Current form, 0·6 sec. after current started.
III. Current form, 0·8 sec. after current started.
IV. Applied P.D. 50 volts. Current density 0·4 amp. per sq. cm.
V. Applied P.D. 24 volts. Current density 0·2 amp. per sq. cm.
VI. Applied P.D. 13 volts. Current density 0·11 amp. per sq. cm.
VII. Effect of adding a trace of sodium chloride to the electrolyte. Other conditions the same as No. VIII.
VIII. Applied P.D. 100 volts. Current density 0·96 amp. per sq. cm. Temperature of electrolyte, 96° C.
IX. Applied P.D. 100 volts. Current density 1·24 amps. per sq. cm. Self-inductance in circuit 20·5 henries.

Except Nos. I., II., and III., the oscillograms were photographed 10 minutes after the current had been started, fresh aluminium being used in each experiment.

CIII. *The J Phenomenon in X-Rays.* (Part I.)

By C. G. Barkla, *F.R.S., University of Edinburgh* [*].

Introduction.

THE investigation of the J phenomenon has led to conclusions of such great interest and wide application that the writer is led to give a more complete and connected account of the subject than has been done hitherto. A number of short summaries and some fragmentary results have already been published [†], but these reports have been very inadequate and cannot have conveyed any idea of the full significance of the experimental results. Though much work has been done and many facts have been learned, the study of the subject has only just begun to yield its most interesting conclusions. It is possible now to see in what direction we are moving, and to realize some of the consequences which necessarily follow, and others which will probably follow from the results of experimental investigation. A great deal of the work which has been done, might have been done much more accurately; we were however looking for large effects, and for results of fundamental importance rather than for accuracy in detail. These large effects we have found, and we now propose to give an account of them in as brief a form as possible. Brevity is indeed essential, for the subject has become too vast for a detailed account before the outlines have been indicated. Let it be said now that the J phenomenon has been observed between one and two hundred times, and without the least uncertainty. It is thus possible to give only a few examples of results obtained from the most interesting and significant experiments which have been undertaken. We should add that if some of these experiments were repeated other observations would be taken based on more complete knowledge of the phenomenon than was possessed at the time the experiments were made. It may, however, be a long time before we have opportunity to repeat all of these.

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[*] Communicated by the Author.

[†] Barkla, 'Bakerian Lecture, 1916,' Phil. Trans. 1917; Barkla & White, Phil. Mag. Oct 1917; Barkla & (Mrs.) Sale, Phil. Mag. April 1923; Barkla, 'Nature,' Nov. 17, 1923, and 'Nature,' Nov. 22, 1924; Barkla & Khastgir, Phil. Mag. Jan. 1925.

The results of experiments which are recorded will suggest many questions,—questions some of which can only be answered after further investigation. In some cases it will probably be wiser to withhold results until definite conclusions have been arrived at, rather than to excite speculation as to the probability of various possible alternatives. But though we are fully conscious of the vastness of the field which needs to be explored we have made definite tracks in many directions. In spite of the incompleteness of these investigations, a great deal of what appears to be of fundamental importance can be told. It is proposed to do this in several communications. A full and profitable discussion of the subject can only be undertaken when the experimental facts have been made known; this we shall proceed to do.

Early Investigations.

When making a study * of the relation between the energy of the K characteristic X-radiation emitted by an element and the number of electrons in the K corpuscular radiation associated with that particular characteristic radiation—a study which led to the conclusion that one quantum of K X-radiation was emitted subsequent to the ejection of each K electron—it was found that a sudden and quite unexpected increase occurred in the ionization in air when the X-rays reached a certain critical frequency, very much higher than the K frequencies for air. As such an increase of ionization had not previously been observed in any gas except in association with the emission by that gaseous substance of a characteristic X-radiation, this suggested the existence of a characteristic radiation of higher frequency than the K radiation—a J characteristic X-radiation.

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* See Bakerian Lecture, 1916.

Further investigation added to the evidence for the existence of such a characteristic radiation, for not only were all the usual accompaniments of the emission of a characteristic radiation observed from light elements, but a secondary radiation of more absorbable type than the primary was actually observed to be emitted; also it was observed only on the higher frequency side of what was approximately the same critical frequency.

Thus as a primary radiation of increasing frequency passed through a substance, while there was in general the usual diminution in absorption, at the critical penetrating power there occurred

(1) a sudden increase in the absorption of the primary X-radiation;
(2) a sudden increase in the ionization in the substance when that substance was in a gaseous state;
(3) an increase in the electronic emission from the substance when that was a solid in the form of a thin plate; and
(4) in the immediate neighbourhood of this critical frequency there appeared from the substance a secondary radiation more absorbable than the primary.

Previous to these experiments *any one* of these phenomena had been observed only in association with the emission of a characteristic radiation, of series K or L. The combination seemed overwhelming evidence for such a radiation, though the transformed radiation had not been shown to be characteristic solely of the element emitting it. It had been found to have features characteristic of the element, but had not been shown to possess a penetrating power characteristic *only* of the element. Especially was the evidence considered sufficiently convincing as the critical frequency varied from substance to substance, increasing with the atomic number of the element, as does the critical frequency associated with the K or the L radiations.

So much was recorded in the Bakerian Lecture for 1916

(Barkla, Phil. Trans. 1917). Since that time the reality of the phenomenon has been confirmed by scores of experiments, yet with all the similarities to the production of X-ray fluorescence, striking differences have appeared; and certain features have been brought to light which make the study of the greatest interest and importance.

It was hoped that long before the present time a more or less satisfactory explanation of the phenomenon might be found; but though much has been learnt and laws have been found, the phenomenon has been strangely elusive. The principal difficulties have arisen from two causes: firstly, the phenomenon is dependent on some factors which we have not yet been able to identify. It quite definitely occurs or does not occur, and we are left in no doubt as to which we are observing. But the feature distinguishing the experiments in which the above phenomena occur and those in which they do not occur, has not been recognized. As the J phenomenon occurs and does not occur under what appear to be identical essential conditions, it becomes exceedingly difficult to study the effect of a variation in conditions which are under control. Secondly, the phenomenon is so remarkable and has features so unlike anything with which we are familiar that nothing can be taken for granted. All the fundamental facts concerned with X-ray scattering and X-ray fluorescence as ordinarily known need to be investigated afresh in connexion with the new phenomenon. The phenomena of scattering and fluorescence, too, have their counterparts in optics, but the J phenomenon seems to open up quite new territory. The investigation is thus difficult for both practical and theoretical reasons; but much needs to be told, for it has an important bearing on many problems; indeed it appears to be intimately connected with that greatest problem of all—the problem of radiation itself. Though we cannot yet give the final solution, a knowledge of the phenomenon is essential if gross misinterpretations of experimental results are to be avoided. We do not propose to give a description of the apparatus used in all experiments—they are far too numerous. And it is not easy to see that much would be gained, for the apparatus and arrangement used in experiments showing the J phenomenon are identical with those in which the J phenomenon at other times did not occur. The results, however, cannot be described as irregularities, for one of the most remarkable features of the phenomenon has been its surprising regularity, when it does occur. The account given in this communication (Part I.) is little more than an introduction to the whole subject.

Absorption Experiments.

Absorption experiments were undertaken in 1915 and 1916 in order to determine if discontinuities occurred corresponding to those previously found in ionization when the ionizing radiations were characteristic radiations of the K series. They showed the discontinuity most markedly. In some of the earliest experiments, however, the radiation experimented upon was the radiation proceeding from an ordinary X-ray tube and filtered so as to eliminate the soft constituents. The pressure of the gas in the tube was varied and the thickness of filters altered so that the radiation used was the most penetrating portion of that emitted from the tube at different pressures. It was found by successive absorptions to be comparatively homogeneous. As the pressure of gas in the tube was reduced there was in general an increase in the penetrating power of the radiation emitted. The absorption in a given substance, however, exhibited a discontinuity, rising abruptly to a higher level and subsequently diminishing as previously with a diminution in the pressure of the gas in the tube. There was no doubt that the penetrating power and thus the frequency of the rays experimented upon varied steadily, for at the critical point in any substance the absorptions in all other substances progressively diminished as one would expect. But each substance showed its own discontinuity at a critical penetrating power depending upon the substance. Results obtained by Barkla and Miss White were published in the Philosophical Magazine in 1921.

The critical penetrating power was found to increase with the atomic number of the absorbing element.

It should be pointed out that in order to minimize any effects of heterogeneity in the beams experimented upon, a 50 per cent. absorption was always obtained when determining the absorption coefficients, and the absorption was calculated from the equation $I=I_0e^{-\mu x}$ as though the radiation was perfectly homogeneous. The magnitude of the sudden change in the value of $\frac{\mu}{\rho}$ was of the order of 15 per cent. There was not the slightest doubt of the reality of the phenomenon, for the step or discontinuity was quite large and could be traversed repeatedly in either direction; it could not escape observation. Such a step was, of course, quite familiar since the discovery by Barkla and Sadler of the K absorption edge associated with the K characteristic radiation.

Unusual features only very gradually began to appear.

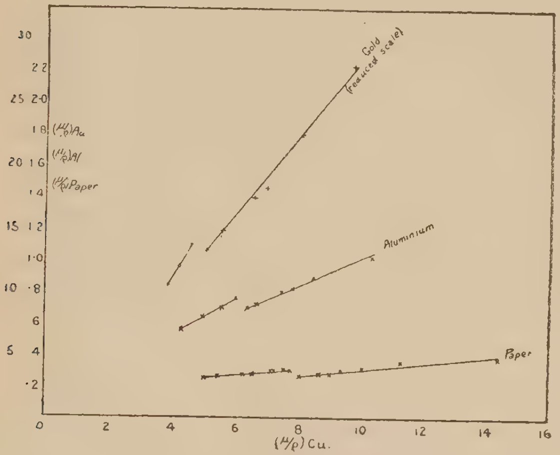
The first noteworthy point was the abruptness of the change in absorption. Other experiments did, it is true, indicate that the radiations used were unusually homogeneous, but from our experience of the K and L absorption discontinuities, we did not expect the change to be quite so sudden. When a heterogeneous beam is gradually hardened up, though the absorption of a homogeneous constituent may be regarded as rising suddenly as it passes the K or L critical absorption frequency, owing to heterogeneity the total absorption rise is gradual; but the J discontinuity was found to be absolutely abrupt even when a very heterogeneous radiation was used. This effect is as though the whole absorbing property of the substance was suddenly increased for every constituent of the complex radiation, and then subsequently the absorption changed in the normal way with increasing frequency, but at the higher absorption level.

In many of the following experiments no attempt was therefore made to produce even approximately homogeneous beams, for these heterogeneous radiations provided us with the phenomenon which we wished to examine. In one set of experiments, for example, the heterogeneous X-radiation scattered from very thick plates of aluminium was used. As the primary beams exciting this radiation varied in penetrating power, the absorption of the scattered radiation was measured in several substances. The discontinuities again appeared exactly as they had done in experiments on primary radiations. The results obtained for the absorption by paper, aluminium, and gold on three consecutive days are shown in fig. 1. This figure should be compared with that published by Barkla and Miss White obtained from their experiments on filtered primary beams direct from an X-ray tube. The agreement in position and magnitude of the discontinuity is remarkably close.

Using such scattered radiations, the discontinuities occurred without interruption for a long period, and we concluded that the scattered radiation was much more susceptible to the phenomenon than was the primary radiation. The two, of course, differed in these respects,—the primary beam necessarily consisted of a few narrow pencils; the scattered radiation was a wide beam: the primary was practically unpolarized; the scattered radiation highly polarized: the primary was comparatively intense; the scattered radiation was feeble.

Later experiments, however, showed that even the scattered radiation did not always exhibit the phenomenon; the discontinuity disappeared and was not observed for a long period. Thus at times the perfectly regular linear relationship between the absorptions in various substances was obtained; at others, though the experimental conditions were apparently identical, the J absorption discontinuities were obtained without the least uncertainty, and at the penetrating powers characteristic of those substances. It thus appeared that there were two possible absorptions in a given substance, some apparently slight change in the conditions of the radiation deciding which absorption would occur.

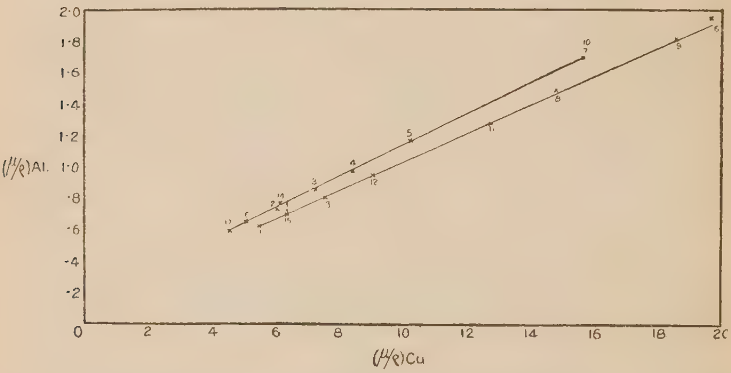
Fig. 1.



It is of course evident that if the controlling factor varied during a series of observations, the discontinuity might occur at any penetrating power within the range of penetrating powers over which there are two possible absorptions. This very rarely happened, however, for above the critical penetrating power the absorptions in a given substance were almost invariably at either the lower or the upper absorption levels, not fluctuating from one to the other, during a series of observations.

Perhaps the most striking exception to this rule which we venture to give is shown in fig. 2, in which absorptions in aluminium are plotted against absorptions in copper. The numbers indicated by the various observational points indicate the order in which the observations were made. They show that though all the points lie fairly accurately on two straight lines, there are in a series of 17 observations as many as 9 changes from one level to the other. The radiation was evidently somewhere about the state of instability between the two different states; it was very sensitive to the unknown controlling factor. This experiment (though it is such an outstanding exception among this particular series) does show that the higher absorbing level may be reached by radiations of frequency considerably lower than the J critical absorption frequency. This conclusion receives ample support from experiments on the scattering of X-rays to be described in later papers. It should be noticed that in the latest observations from 11 onwards, *i. e.* when conditions had apparently settled down, there was the usual sudden rise in the absorption in aluminium at $\frac{\mu}{\rho} = \cdot 7$ approximately*.

Fig. 2.



A remarkable feature then is the fact that the absorption discontinuity occurred so persistently at the same critical penetrating power for a given substance. This may be seen, for instance, from the various figures in this paper, though they are selected to illustrate different points. The discontinuity in aluminium is at a value of $\frac{\mu}{\rho}$ in Al of 0·7,—this being calculated from a 50 per cent. absorption. This has been observed more than 30 times, that is in over 30 distinct experiments, in many of which the step was traversed several times in both directions.

As previously stated, the position of the absorption step depends upon the atomic number of the absorbing element, an increase in the atomic number being accompanied by a displacement of the absorption step towards the more penetrating end of the spectrum ; that is, by an increase in the critical absorption frequency—a result agreeing with that originally obtained by Barkla & Sadler for the K absorption edges. The J discontinuity did not, however, occur nearly so frequently in copper as in aluminium—the only two substances upon which the numbers of experiments were comparable,—consequently in plotting the results the absorption in copper was usually taken as the standard.

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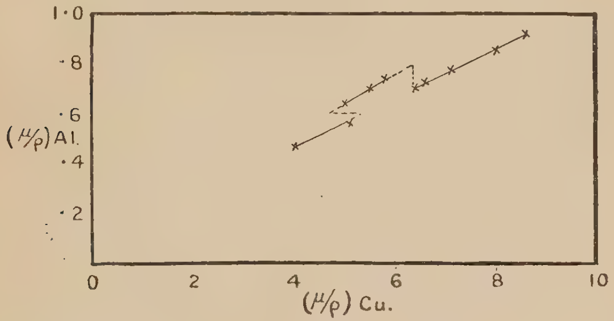
* See observational points, 11, 12, 13, 14, 15, 16, and 17 in fig. 2.

Fig. 3 shows the result of one experiment in which both aluminium and copper showed the discontinuity,—when the relative absorptions returned to the original line approximately. (Without other evidence it might be thought that the absorption in aluminium returned to the lower level again : the absorption in aluminium, however, varied progressively with the gas pressure in the X-ray tube throughout the copper discontinuity.)

Fig. 3.

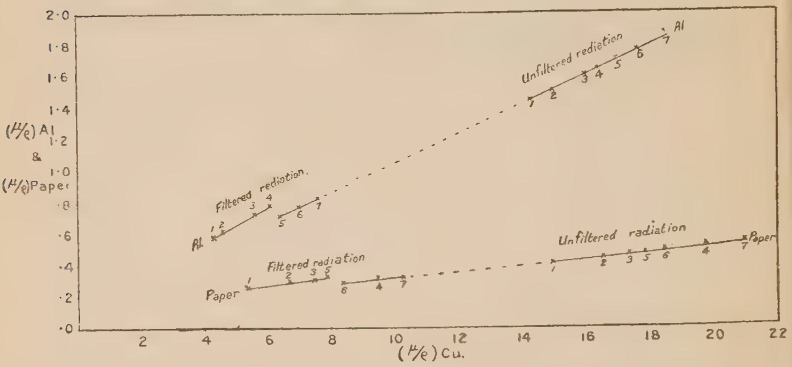


Such discontinuities have been found in all substances tested, *i. e.* by the absorption method in carbon (in paraffin wax), oxygen (in water and in paper), aluminium, copper, platinum, and gold ; and by other methods in nitrogen, sulphur, and lead.

Another remarkable feature of the phenomenon is that with beams obtained in so many different ways the critical penetrating power should appear so constant. In fact, the discontinuity appears to depend more closely upon the absorption coefficient of the radiation than upon mere wave-length. This is illustrated very distinctly in several ways.

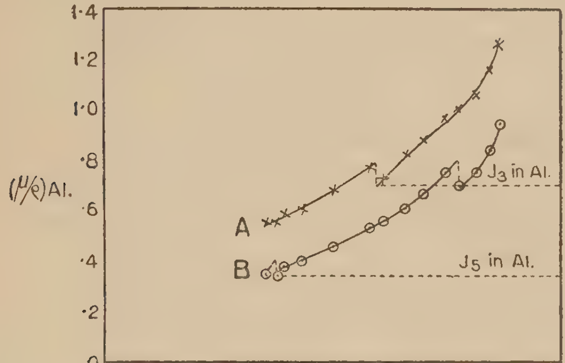
Thus a heterogeneous beam direct from an X-ray tube when gradually made more penetrating may exhibit no absorption discontinuity, whereas the same beam when filtered and so brought to a higher average penetrating power shows the discontinuity quite clearly and at the correct critical point. Thus fig. 4 shows two absorption curves, the upper one for aluminium, the other for paper. The upper curve shows in its right branch the relation between absorption in aluminium and absorption in copper for a beam direct from an X-ray tube. The left branch, which it will be observed is broken into two sections, shows the relationship between the two same quantities when the primary beam had been filtered by ·0058 cm. of copper; the filtered beams of course were of much higher average penetrating power than the unintercepted beams. The results of absorption experiments on the same beams unintercepted and filtered are indicated by the same number

Fig. 4.



on the figure; thus (1) on the curve for the filtered portion corresponds to (1) on the curve for the unintercepted. As the tube was hardened progressively from 7 to 1 there was a progressive fall in the absorption of the unintercepted beam by aluminium, but the filtered beam exhibited a sudden increase in the absorption from the state 5 to the state 4 (see figure). According to all accepted ideas every constituent in the filtered beam was also in the unintercepted beam, yet the absorption step was not indicated to the slightest extent in the unintercepted beam. It should be noticed that the discontinuity occurred at the same point—*i. e.* the same value of the absorption coefficient in aluminium $\left(\frac{\mu}{\rho}=\cdot 7\right)$—as in the results shown in fig. 1 for the scattered and otherwise unfiltered beams. The lower curve in fig. 4 shows the corresponding phenomenon in paper. In this case again the discontinuity appeared in the absorption (by paper) of the filtered beam and not of the unintercepted beam; but it occurred at the absorption coefficient characteristic of paper and agreeing with the results of experiments obtained by Barkla & White with primary beams and those already recorded in this paper and made upon scattered beams.

Fig. 5.



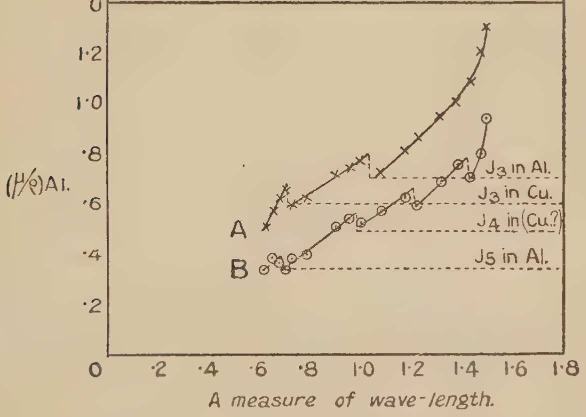


Fig. 6.

Again, two beams proceeding from the same tube at the same time in different directions may have different penetrating powers. (We did not investigate the cause of this; there were various possibilities. These did not appear of any special interest at the time, though now we find there is strong evidence that the difference is itself associated with the J phenomenon; it is like the difference between a primary and a scattered radiation as frequently observed.) As the tube hardens up, the absorption step or discontinuity occurs in each beam when that particular beam reaches the critical penetrating power, and not when the tube reaches a certain state or begins to emit certain rays. This is illustrated in fig. 5, in which the two curves A and B show by their ordinates the absorption coefficient in aluminium of the two beams from the same tube. The abscissæ give a rough measure of the effective wave-length of radiation proceeding from the tube. (It is unnecessary to indicate the method of measurement; it was based on the path of the electrons ejected by this radiation.) Beginning at the right-hand side both curves show the progressive diminution in the absorption by aluminium as the effective wave-length is diminished, except at the critical point $\frac{\mu}{\rho}$ in aluminium $= \cdot 7$ (and much less clearly though perhaps not less markedly at the value of $\frac{\mu}{\rho} = \cdot 33$ approximately). Each beam, when its absorbability reached the critical value represented by $\left(\frac{\mu}{\rho}\right)_{\mathrm{Al}} = \cdot 7$, showed a marked increase in the absorbability. For the softer radiation (the upper curve) the tube was in a harder state than for the other before it showed the absorption rise,—that is, the rise in absorption appeared not for a given state of the tube, but when a given penetrating power was reached. It should be stated that the beams had both been filtered by a constant thickness of about ·5 cm. of aluminium.

Fig. 6 shows the results obtained immediately afterwards under similar conditions except that the radiations were filtered by ·0141 cm. of copper instead of ·5 cm. of aluminium before being absorbed by aluminium. The features of fig. 5 appeared again, and in addition another discontinuity in both curves,—in this case the discontinuity in copper, for it occurred at precisely the penetrating power found for copper in other experiments. Thus as a radiation of increasing frequency from an X-ray tube was transmitted through copper, at the critical point for copper there occurred an increase in the absorbability in a second substance (aluminium).

Thus the radiation which exhibited the characteristic increase in absorption in copper was after transmission through copper more absorbable to aluminium also. This was additional to the change which took place in aluminium itself. The radiation was thus by its passage through copper truly transformed; its properties were changed in such a way as to make it more absorbable in some substances at least.

Fig. 7 was obtained in a similar way to fig. 5 and a few days subsequently. The discontinuities had entirely disappeared.

Further, in some cases, the discontinuity is not observed when thin sheets, absorbing only a small fraction of a beam, are used to measure the absorption coefficient, whereas thick absorbing sheets exhibit the discontinuity. This is illustrated in fig. 8, in which the lower graph shows the values obtained by using the thickness of absorbing material which cut off

Fig. 7.

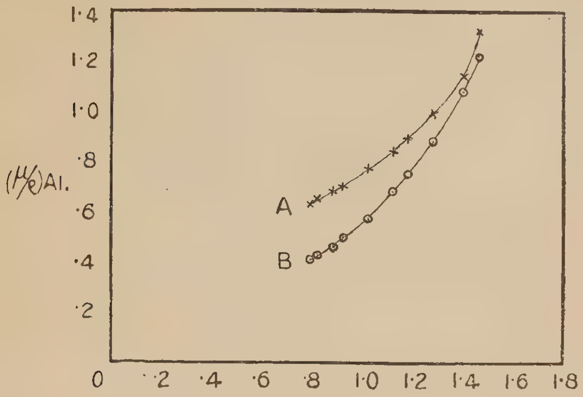
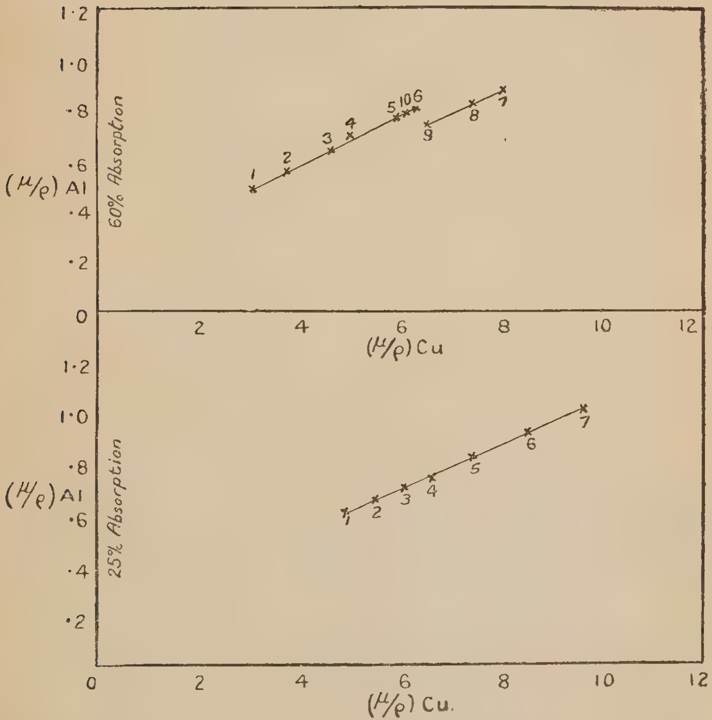


Fig. 8.



only 25 per cent. of the radiation, or more precisely 25 per cent. of the ionization produced by the radiation, while the upper graph was obtained from measurements in which as much as 60 per cent. was absorbed. The rise to the higher level of absorption in aluminium appeared only in the 60 per cent. absorption graph. The straight line on the graph for 25 per cent. absorptions is precisely a continuation of the lower branch obtained in the 60 per cent. absorption. It is evident then that the discontinuity must occur at some critical thickness of the absorbing sheets.

Fig. 9.

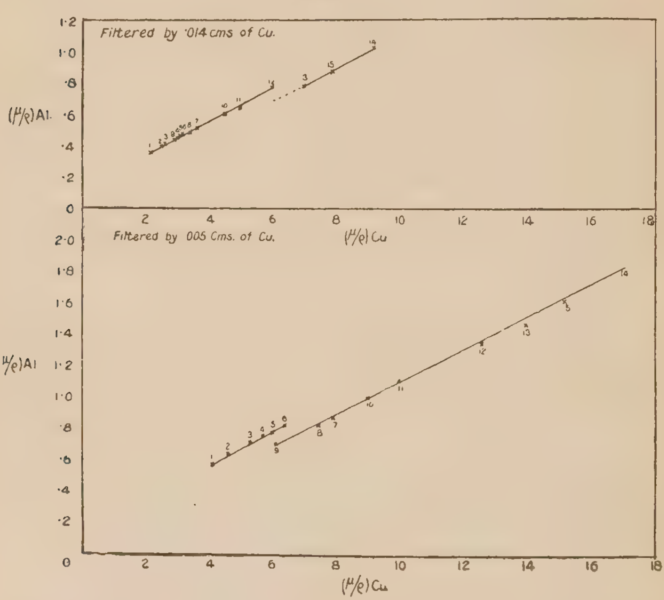
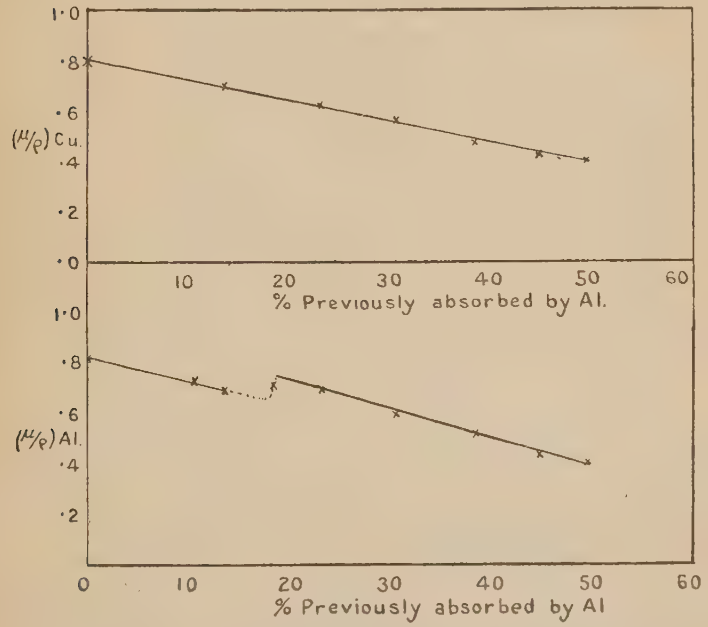


Fig. 9 shows the relation between absorption in aluminium and absorption in copper for the same radiation filtered by two different thicknesses of copper. In this case, however, the thickness of the absorbing sheet (by which the 'absorption coefficient' was determined) was the same in both cases. The lower graph gives the relation for the beam transmitted through ·005 cm. of copper, and the upper graph for the same radiations transmitted through ·014 cm. Corresponding numbers on the two graphs indicate radiations which were identical before transmission through these differing thicknesses of copper. Commencing at the low frequency end and gradually increasing the frequency, *i. e.* moving from right to left of the figure, the discontinuity appeared very early for the beam transmitted through thick copper, and much later for the beam transmitted through the thin sheets. But in both cases it occurred when the average value of $\frac{\mu}{\rho}$ in aluminium reached the value 0·7. Again, according to present ideas, this is a strange result, for the radiations at which the discontinuities occurred were presumably of quite different character; what was common was a certain rate of absorption as measured by ionization methods. The two curves superpose perfectly, giving the one discontinuity.

Fig. 10.



Such results led to an examination of the effects of successive thin filtering sheets on a heterogeneous radiation. The average absorption coefficient calculated from the relation $I = I_0 e^{-\mu x}$ (as though the radiation were homogeneous) was determined after the radiation had been transmitted hrough increasing thicknesses of aluminium. Thus in fig. 10 the value of $\frac{\mu}{\rho}$ in aluminium and $\frac{\mu}{\rho}$ in copper (calculated as indicated) are plotted against the amount of radiation previously absorbed by aluminium—as measured simply by diminution of ionization produced by the beam in an ionization chamber. In one case the discontinuity is shown by the rise in the absorption in aluminium, while in the other case the absorption in copper even after transmission through the same thickness of filtering aluminium shows no sudden increase. This indicates that the discontinuity occurred not in the process of filtering but in the final absorbing sheets by which the absorbability was tested. The filtering sheets were, however, essential to the discontinuity found in the absorbing sheets. (At the time of the experiment we did not realize that the discontinuity would not have occurred at the critical point indicated except for the last thin layer of the absorbing sheet.)

Fig. 11.

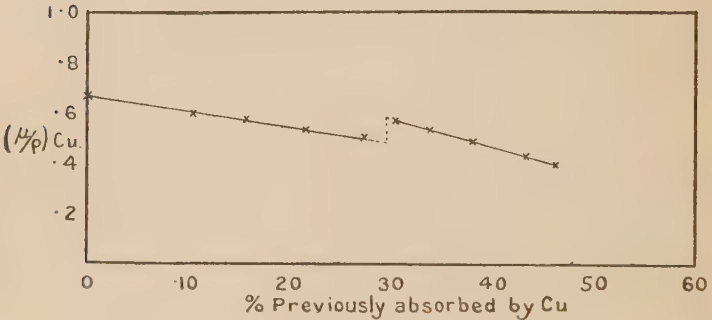


Fig. 11 shows a corresponding discontinuity in the absorption in copper when the primary beam was filtered by copper. Again, this appeared at the critical absorption coefficient characteristic of copper,

Thus as a heterogeneous primary beam is increased in penetrating power as a whole, or even has its average penetrating power increased by the process of filtering, there occurs an abrupt increase in the absorbability of the radiation in a particular substance. The critical penetrating power at which the discontinuity occurs is characteristic of the absorbing element. The transmitted beam is, however, subsequently more absorbable in other substances also. The critical penetrating power varies only very slowly with the atomic number of the absorbing element, but it is in the same direction as for the K, L, or M absorption edges.

The following values have been obtained for the position of the J absorption steps in C, O, Al, Cu, Pt, Au, these being expressed as mass absorption coefficients in Al, and in approximate wave-lengths :—

J_3 Absorption Steps.

Approximate Absorption Coefficients $\left(\frac{\mu}{\rho}\right)_{\mathrm{Al}}$

	C.	O.	Al.	Cu.	Pt.	Au.
Barkla & White ……	1·05	0·84	·7	<·6>·54	—	—
Barkla & Stevens …	—	·82	·7	·6	·57*	·54*

Approximate Wave-lengths †—Ångström Units.

C.	O.	Al.	Cu.	Pt.	Au.
·39	·355	·335	·315	·305	·30

* Reduced to the lower level.

† Converted to wave-lengths from S. J. M. Allen's table (Phys. Rev. July 1924).

Though these discontinuities have been obtained in this laboratory by several experimenters the agreement between the values is remarkably close.

All the radiations experimented upon were the primary rays from an X-ray tube, filtered by aluminium or copper in order to eliminate the softer constituents ; or they were X-rays scattered from thick sheets of light substances. These discontinuities were first studied with the help of Dr. Margaret White ; some of the results were recorded in a paper by Barkla & White (Phil. Mag. Oct. 1917). It was afterwards observed that the discontinuites had appeared in the results of earlier experiments, but as the results were used for other purposes the discontinuities had passed unnoticed. All the results exhibited in this paper were obtained with Mr. Stevens. The discontinuities of this particular series J_3 have been observed between 70 and 80 times under various conditions ‡.

The much more homogeneous rays constituting the characteristic radiations of the K series have also been experimented upon, and similar discontinuities have been found in the absorption of these—as recorded in the Bakerian

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‡ The J_3 absorption step in aluminium was obtained by the spectrometer by Dauvillier (*Annales de Physique*, vol. xiii., 1920) for a wave-length ·358 Å.U. The agreement is probably as close as the accuracy of the relation between absorption-coefficient and wave-length will permit.

Lecture for 1916 (Phil. Trans. 1917). Initially there appeared to be a discrepancy between the values of the critical mass-absorption-coefficient obtained for these characteristic rays and those given above under the heading J_3 and obtained from experiments on more heterogeneous primary rays. It was seen, however, that the difference between the critical values of $\left(\frac{\mu}{\rho}\right)_{\text{Al}}$ for the primary radiation and for the fluorescent characteristic radiation was quite a consistent one. In fact, the positions of the absorption steps obtained by using characteristic radiations seemed to be just those obtained by primary rays shifted along towards the longer wave-length end of the spectrum by 20 per cent. to 25 per cent. increase of wave-length. It originally appeared probable that this discrepancy was due to the difference in the constitution of the two beams—one a primary, giving presumably a continuous spectrum within narrow limits, and the other the characteristic radiation giving a line spectrum approximately consisting of radiations of two neighbouring wave-lengths. Fortunately, however, such a complication does not appear to express the truth, for we have found that these two form quite distinct series and may *both* be obtained in experiments upon certain radiations (Barkla & Khastgir: unpublished).

The only values in this series obtained from direct absorption experiments upon characteristic radiations are those for oxygen and aluminium. Sulphur and copper discontinuities have also been obtained using characteristic radiations, but they have been by ionization methods—methods indeed which are much more sensitive than the absorption method. But of these more later. The values obtained with Dr. Khastgir on heterogeneous scattered X-rays are also given under the heading J_2. Thus the J_2 discontinuities were first observed in work with Mr. Hagger; these were ionization discontinuities. The J_2 absorption discontinuities and the corpuscular emission discontinuities were searched for and found with Dr. Margaret White. These were all in experiments on characteristic radiations of the K series. They have since been observed in experiments with Dr. Khastgir on the absorption of more heterogeneous scattered radiations, and apparently by E. A. Owen and by C. M. Williams, using the more homogeneous radiations obtained by the spectrometer (Proc. Roy. Soc. A, xciv., 1917).

The various values obtained are given below :—

J_2 Absorption Steps.

Approximate Absorption Coefficients $\left(\frac{\mu}{\rho}\right)_{Al}$

	N.	O.	Al.	Si.	S.	Cu.
Barkla, White, & Hagger	2·5	2·5 to 2·2	1·8	—	1·7	—
Barkla & Khastgir...	—	2	1·8	—	—	(2·3?)
C. M. Williams	—	—	2	—	—	1·46*
E. A. Owen	—	—	—	1·85*	—	—
Approximate Wave-lengths—Ångström Units.	·55	·5	·49	·493	·48	·45

* Obtained from wave-lengths given in papers by E. A. Owen and by Williams.

Again, a further series of absorption discontinuities has been found in experiments with Dr. Khastgir upon the secondary X-rays scattered from light substances. These are in the region of more absorbable radiations—lower frequencies. These are indicated below :—

J_1 Absorption Steps.

Approximate Absorption Coefficient $\left(\frac{\mu}{\rho}\right)_{Al}$

	O.	Al.	S.
	>4	3·8	3·5
Approximate Wave-lengths—Ångström Units.	>·66	·63	·61

Also in addition to the above we have previously recorded similar absorption discontinuities for the elements carbon and oxygen at a value of $\left(\frac{\mu}{\rho}\right)_{Cu}$ of about 3·5 corresponding to a value of $\left(\frac{\mu}{\rho}\right)_{Al}$ equal to about 0·47 or to a wave-length of 0·28 Ångström units. There appears to be little doubt then of a similar series of discontinuities in this region. This J_4 series is what Barkla & White referred to as a possible I series when it appeared that only one J series was known.

And finally, quite independent discontinuities have been observed in aluminium at a value of $\left(\frac{\mu}{\rho}\right)_{Al} = ·34$ or a wave-length of approximately ·23 Å.U.† These are shown in figs. 5 & 6 and appear in other experimental results.

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† Dauvillier gave evidence for a value ·228 Å.U. in Bromine.

Thus there have been observed what appear to be three distinct series of these J absorption discontinuities, and what are probably isolated results in two further series. We have been in the habit of distinguishing between them by describing them as the first or second and so on, and for the present we shall name them the J_1, J_2, J_3, J_4, J_5 steps, J_1 being among moderately soft radiations (say about ·6 Å.U.) ; the J_2 among the slightly more penetrating radiations and in the neighbourhood of ·5 Å.U.; J_3 the series given by Barkla and White and in the neighbourhood of ·3 to ·4 Å.U.; and others in the region of high frequencies and between ·2 and ·3 Å.U.

No high degree of accuracy is claimed for these values of critical absorption coefficients or their equivalents in wavelengths. When a heterogeneous radiation is being experimented upon, it is probably the value of $-\frac{1}{I\rho}\frac{dI}{dx}$ just before the discontinuity occurs that should be determined. But our method gives a result which usually differs little from this. And of course when the discontinuity occurs, absorption coefficient as calculated ceases to have any precise meaning. Further, even away from a discontinuity the absorption coefficient does not define the radiation—it is not unique. But these are all points for a later paper, when the broader facts have been outlined.

Critical Conditions.

Attempts to discover the difference between the conditions of experiments which showed, and those which did not show the J phenomenon, have so far been unsuccessful.

The J phenomenon occurs sometimes and at other times does not occur with strong, and with very feeble radiations ; with highly polarized, and with unpolarized radiations ; with narrow pencils of radiation such as would produce an ionization almost entirely outside the radiation, and with wide beams producing the bulk of its ions within that beam ; with heterogeneous radiations, and with approximately homogeneous radiations ; with radiations from many different tubes, and with different anticathodes ; with primary radiations, scattered radiations, and characteristic radiations. Various methods of measuring the intensity of the Röntgen radiation have been adopted. Ionization in air, in sulphur dioxide, and in hydrogen, produced by the emission of high-speed electrons from an aluminium plate in the path of the X-rays, and ionization produced by high-speed electrons ejected from copper, have all been used to measure the intensity.

The discontinuity has been observed by each of these methods and at the same critical penetrating power. It should be noted, however, that all such methods of measuring an X-radiation are based on what is admittedly an action of X-rays governed by quantum laws. All directly observable actions are probably governed by such laws. We must therefore for the present regard all such measurements as measurements of the X-rays themselves. We shall, however, have more to say of this in later papers.

We have observed the effect with a dozen or more arrangements of apparatus. Though we have frequently looked for effects produced by a change of X-ray tube or by its method of excitation, by changes of absorbing material—replacing absorbing sheets after prolonged exposure to X-rays by quite fresh and previously unexposed sheets,—we have never observed any evidence of dependence on these things. Sometimes the J discontinuity occurred day after day; at other times it could not be observed for a comparable period. More remarkably still, at certain times the J effect appeared and disappeared before our eyes, while we were unable to detect any change in the conditions. Further experiments on this point will be described later.

Thus though heterogeneity or feebleness or polarization may be favourable to the phenomenon, not one of these factors is essential. Neither can the critical factor be essentially in the absorbing substance, for reasons given above.

The critical condition appears then to be provided either by the X-radiation or by something with the X-radiation or by some external influence superposed upon the radiation.

Comparison with other Absorption Discontinuities.

It will have been observed that this J absorption phenomenon, though superficially so like the K absorption phenomenon associated with the emission of K characteristic radiation, has many unique characteristics which are of the greatest importance theoretically. There are, indeed, many features which distinguish it from anything previously known. The most striking are the following:—

1. The phenomenon is conditional on some factor or factors which have never previously been considered as a governing factor in X-ray phenomena. The only condition essential to X-ray fluorescence and the accompanying K, L, or M absorption phenomenon is (as far as has been discovered) that the radiation should possess some constituent of frequency

greater than the critical absorption frequency (Stokes' law)*.

2. The sudden changes in absorption occur with surprising abruptness; indeed there appears to be an absolute discontinuity as though every constituent of the radiation being absorbed were suddenly absorbed at a higher level. In fact, the discontinuity in absorption appears to be quite as perfect when a heterogeneous beam is used as when the most homogeneous radiation is employed. Thus if the constituents were independent, the rise in absorption would be very gradual, occurring for each constituent as it passed the critical absorption frequency.

3. The discontinuity is much more closely associated with an absorption coefficient than with a certain wave-length.

According to all present conceptions, the filtered radiation contains the same constituents as the unfiltered though in different proportions, yet frequently only the filtered radiation shows the discontinuity. Change in intensity (alone and of the magnitude produced by filtering) has not been found to produce the result ; it is due to a change in the properties of the radiation produced by transmission through matter.

4. When the rise of absorption has occurred in a substance, the transmitted radiation is found to be more absorbable in other substances quite independently of the fact that these other substances exhibit their own absorption discontinuity (increased absorption). Thus the transmitted radiation is a transformed radiation as far as its penetrating power is concerned.

5. The change of critical absorption coefficient with atomic number of the absorbing substance is very small and diminishes with increasing atomic number.

6. The series of critical absorption coefficients in the various elements cuts right across the well-known K series.

Summary.

The paper gives a brief general account of the J absorption discontinuities with a few illustrations of the results obtained. They show that as the penetrating power of a radiation is increased either (1) by increasing the speed of the electrons which excite it, (2) by selection of the characteristic radiations from elements of increasing atomic number, or (3) even by the process of filtering a heterogeneous radiation, there occur sudden increases in the absorption of the radiation by any particular substance.

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* First stated by the writer for X-rays in 1909, Proc. Phil. Soc. Camb.

In the first two cases this is very similar to the rise in the absorption in a substance accompanying the emission by that substance of a characteristic radiation; but the production of the effect by mere filtering is a result of quite a new kind. It will be discussed when other results have been described. This absorption discontinuity occurs at higher frequencies (higher penetrating powers), the higher the atomic number of the absorbing element.

Absorption discontinuities have been observed directly in carbon, oxygen, aluminium, copper, platinum, and gold; and indirectly—by the accompanying ionization—in nitrogen, sulphur, and lead. They all fall into several series, J_1, J_2, J_3, and there are isolated cases indicating further probable series, J_4 and J_5.

It has already been shown, and will be further shown in a later paper, that the increase in absorption is accompanied by the emission of slowly moving electrons from the absorbing substance, producing, when that substance is in a gaseous state, an even more strongly marked discontinuity in ionization.

Features distinguishing the sudden rise in absorption from that accompanying the emission of a K or an L characteristic radiation are given.

Some of the most remarkable conclusions from the experiments are the following:—

There are alternative absorptions possible for what are *to all appearance*—*i. e.* from close examination by other methods—identical radiations. Corresponding to these alternative absorptions there are alternative corpuscular emissions and alternative ionizations in the substances exposed to the X-rays. Indeed the actions of X-rays (which means the quantum actions, for the actions referred to are governed by the quantum laws) depend upon factors other than wave-length of a radiation and the atomic number of the substance traversed. In other words, the activity of an X-ray radiation is dependent on factors which have hitherto not been taken into consideration.

(This paper definitely shows only two levels of activity; it indicates the existence of several, the complete evidence for which will be given later.)

Thus the emission of electrons—the photoelectric effect of X-rays—for rays of a given wave-length is not proportional to intensity; other factors are operative. In fact, experiments seem to show that as far as the J phenomenon is concerned the penetrating power of a complex radiation is a more fundamental quantity than the wave-length or the wave-lengths of its constituents. The phenomenon appears to suggest the separation of the quantum actions of radiation from the frequency of radiation.

The results of more detailed investigation and a more critical discussion will follow.

In conclusion I wish to express my great indebtedness to Mr. W. H. Stevens for his invaluable assistance in all the experimental work, the results of which are recorded in this paper.

[To be continued.]

CIV. *On Eddington's Natural Unit of the Field.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I REGRET that in a paper contributed to your Journal [No. 290 (Feb.), pp. 457–463] I made a serious blunder, to which Dr. Silberstein has kindly called my attention in a private communication. On page 461 I state that recent investigation has increased the estimated value of R, the world curvature-radius, from the order 10^7 parsecs to a much higher order, and in particular refer to an estimate of Dr. Silberstein's of the order 10^{12} *parsecs*. Actually the values derived by him are of the order 10^{12} *astronomical units* (6×10^{12} astr. units by one method, $7{\cdot}2 \times 10^{12}$ by another). The order of magnitude for R is thus much the same as before, and this mistake on my part completely destroys any numerical support for my equation (7) and renders the particular speculation on page 462 quite valueless.

May I, however, point out that Dr. Silberstein's value of $7{\cdot}2 \times 10^{12}$ astr. units for R produces a remarkable numerical coincidence with regard to another speculation concerning "*h*." On page 380 of my book on 'Relativity' I have drawn attention to the fact that if one multiplies the energy-density of Eddington's unit-field by the volume of the electron and, taking this as a unit of energy, multiplies it by the "cosmic" unit of time R/c, the result is a unit of action of the order 10^{-27} if R is assumed to be of the order 10^7 parsecs. Owing to my foolish mistake concerning Dr. Silberstein's value of R, I believed that all numerical support for such an idea had gone (and was thus led to the suggestion made in the paper); whereas I find that, on the contrary, the actual value fits the speculation quite well. In fact, if one takes the unit of action calculated in the manner above to be equal to h, it is easy to derive the equation

$$\frac{r^2}{R\rho}=6\frac{hc}{e^2},$$

which replaces equation (7) of my paper. Now, the right-hand side is 6×861 or 5,166; and if we adopt these values,

$$r=1{\cdot}88\times 10^{-13},$$

$$\rho=\kappa m=7{\cdot}4\times 10^{-29}\times 9\times 10^{-28}=6{\cdot}66\times 10^{-56}\text{ cm.},$$

$$R=7{\cdot}2\times 10^{12}\text{ astr. units}=1{\cdot}06\times 10^{26}\text{ cm.},$$

the left-hand side works out practically 5,000.

I ought to state also that the order of magnitude of the unit-field is an electrostatic unit, not the much smaller value mentioned in the paper.

Yours faithfully,
J. Rice.

George Holt Physics Laboratory,
The University of Liverpool.
March 25, 1925.

CV. *Low-voltage Arcs in Sodium and Potassium Vapours.*

By F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter*[*].

1. *Introduction.*

It is now a well-known fact that arcs may be established in most vapours bombarded by electrons, the energy of these electrons being considerably less than that which would be expected on the quantum theory. In some cases the required voltage between the electrodes is only slightly greater than the resonance potential of the vapour, a correction factor being applied for the initial kinetic energy of the electrons emitted from the incandescent filament cathode. R. W. Wood and S. Okano[†], who carried out an extensive series of experiments with sodium vapour, concluded that the D lines appeared when the potential between the hot cathode and the anode was as low as 0·5 volt, and various experiments showed that the emission of the D lines, under

[*] Communicated by the Author.

[†] Phil. Mag. xxxiv. p. 177 (1917).

these circumstances, could not be ascribed to any secondary action, such as the light from the incandescent filament. Such a result would appear to be in conflict with the quantum theory—namely, that the ionization potential is given by $V=\frac{(1s)h}{e}$ where $1s$ is the frequency of the shortest wave-length in the principal series $\nu = 1s - mp$; but there are at least three factors which must be taken into account in explaining the striking and maintenance of arcs below the ionization potential.

The valency electron, within the atom, may be ejected from the normal orbit to the adjacent outer orbit by an inelastic collision with a bombarding electron, and, while the atom is in this excited or abnormal condition, a second collision with another bombarding electron may occur which results in the complete ejection of the valency electron from the atom. In the case of sodium, for example, the atom may be bombarded by an electron of energy corresponding to 2·12 volts—the resonance potential of sodium vapour—and while it is in the excited state, collision with another electron raises the valency electron to a higher energy level, or outer orbit, ultimately producing ionization. It is evident that the probability of ionization by successive impacts in this manner depends upon the average time-interval within which the excited atoms remain in the abnormal state. From Stark's work * on helium this time-interval appears to be 10^{-8} sec. approximately.

Another controlling factor in the operation of low-voltage arcs is the phenomenon of the absorption of radiation which is emitted when the atoms resume their normal conditions. The valency electron, in a sodium atom, returning to the $1s$ orbit from the $2p$ orbit will give rise to the D-line radiation, which may be absorbed by any neighbouring sodium atom, resulting in the ejection of the valency electron in this latter atom to the $2p$ orbit. The excited atom, thus formed, may then collide with another bombarding electron which completely ionizes the atom. The radiation $1s-2p$, emitted in the first instance, may be diffused throughout the vapour in all directions and, as K. T. Compton † has shown, this ionization, by what he terms "photo-impact," is relatively of far greater importance, especially at high vapour pressures, than ionization by successive impacts. Ionization by "photo-impact" may be the result of several such

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* *Ann. d. Phys.* xlix. p. 731 (1916).

† Phys. Rev. xx. p. 296 (1922).

radiation absorptions followed by a single electron impact of energy corresponding to the resonance potential, so that in this case it would be possible to produce complete ionization of the vapour with electrons none of which have a velocity greater than that corresponding to the resonance potential. In actual practice the striking voltage of the arc should be equal to the difference between the minimum ionizing and resonance potentials, less the average emission energy of the electrons from the cathode, this energy being expressed in volts. The time-interval during which the atom remains in the excited state, *i. e.*, during which the valency electron is in the $2p$ orbit, is not known with any degree of accuracy, as the direct experimental data are very meagre, and give no information as to whether this time-interval is the same for resonance as for other radiation. Kannenstine*, working with helium arcs, found that excited atoms could be detected as long as $2 \cdot 4 \times 10^{-3}$ sec. after the exciting voltage had been removed; and this must be the time during which the individual atoms persist in the excited state. It is probable, however, that this interval, as noted by Kannenstine, represents the time required for the resonance radiation to escape from the gas by a process similar to diffusion, and so this time-interval may represent the summation of the intervals for many thousands of absorptions and re-emissions of radiation.

It is also probable, as suggested by F. Horton and Miss A. C. Davies † as a result of their experiments with helium, that a second stage in the ionization may be brought about by the absorption of radiation from neighbouring impacts. If this second type of resonance radiation exists, and if it is capable of ionizing atoms already in the excited state owing to absorption of the first type of resonance radiation, it is to be expected that this effect would be more marked in completing ionization than impacts, for the same reason that radiation is more effective in displacing the valency electron to the $2p$ orbit than impacts. It appears that the complete ionization observed in low-voltage arcs, operated below the ionization potential, is accomplished mainly with the aid of the "photo-impact" effect.

In connexion with the spectroscopic study of low-voltage arcs in sodium and potassium vapours it was thought desirable to investigate the experimental conditions required for the production of such arcs.

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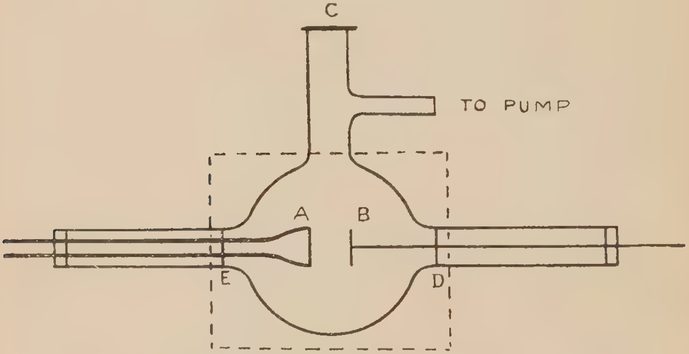
* Astrophys. Journ. lv. p. 345 (1922).

† Phil. Mag. xlii. p. 746 (1921).

2. *Experimental Arrangements.*

The form of tube which gave regular and consistent results is that shown in fig. 1. It was made of silica and had three branch tubes, one of which was used as a means of communication with a rotary oil-pump. A quartz plate C, waxed to the end of this branch, permitted visual observations of the emitted arc spectra. The anode B, a platinum disk whose plane was at right angles to the axis of the discharge-tube, was connected, electrically, to the pool of alkali metal placed at the bottom of the bulb by means of a short iron chain. It was found that such an arrangement assisted the maintenance of steady arcs once they had been started. The incandescent cathode A consisted of three lime-coated platinum strips or, in some experiments, three tungsten wires, arranged in parallel. In this manner a copious supply of electrons was emitted, using fairly heavy currents, without having an unduly large fall of potential across the ends of the incandescent filament. The lead-in wires, entering through ebonite plugs, were of iron and, having fairly large cross-sections, their resistances were practically negligible. These lead-in wires also passed through plates of glass E and D, which, fitting closely to the sides of the tube, minimized vapour condensation with its attendant liability to short-circuit the lead-in wires. The bulb, at the bottom of which was placed the metal, was heated by an electric furnace, the vapour in the discharge-tube being maintained at any selected temperature and pressure.

Fig. 1.



The negative terminals of the heating and anode voltage batteries were connected, and the potential difference between the hot cathode and anode, necessary to strike and maintain the arc, was measured by means of a voltmeter placed between B and the negative terminal of A, from which it will be seen that the readings obtained represented the maximum potential difference, and included any potential fall along the cathode.

In all experiments the distance between the platinum anode and the cathode was, approximately, 3 mm.

3. *Experiments with Sodium Vapour.*

With the cathode maintained at a definite and fixed temperature the voltage necessary to strike the arc gradually decreased as the furnace temperature, and so the vapour-pressure, increased. This was so whether tungsten wires or platinum strips were used, but in all cases the arcing potentials obtained with the tungsten filaments were slightly lower than those given with the platinum. This was due, probably, to the fact that it is impossible to heat platinum to such a high temperature as tungsten, and accordingly the number and speed of the emitted electrons are both greater with the tungsten. Some of the results obtained are shown in Table I., the filament in each set of experiments being intensely bright.

TABLE I.

Tungsten filament.

Furnace temperature.	Arc struck at	Arc maintained at
241° C.	8·2 volts.	7·8 volts.
315°	6·4	5·8
366°	5·8	5·1
426°	5·1	4·1
493°	4·0	2·9

Lime-coated platinum filament.

Furnace temperature.	Arc struck at	Arc maintained at
247° C.	10·5 volts.	10·1 volts.
312°	8·3	7·8
370°	7·1	6·5
428°	6·3	5·2
491°	5·4	4·1

As the filament temperature was raised, the potentials required to strike and maintain the arc decreased, which fact may be explained by the speed and number of the electrons emitted both increasing at the higher temperatures. The arc would start easily at 3·8 volts with the cathode intensely bright, the furnace temperature being 450° C., and this arc was maintained with 2·8 volts. It was possible, also, to strike the arc, after waiting 3 minutes, at 3·2 volts, but with lower potentials it would not start, even after waiting for several minutes. Very few readings could be taken with the filament at the high temperature necessary for such low potentials before the cathode fused and had to be renewed.

In another set of experiments a certain potential was applied which was not sufficient to start the arc. The filament current was then increased, and the value of this current noted when the arc became visible. The results obtained in this manner were not consistent.

Table II. gives the striking and maintenance potentials with various currents passed through tungsten filaments, the temperature of the furnace being 450° C. in every case.

TABLE II.

Filament current.	Arc struck at	Arc maintained at
10·4 amp.	4·3 volts.	3·1 volts.
9·9	4·9	3·8
9·3	5·4	4·5
8·5	5·9	5·2
7·9	6·5	6·0
7·0	7·1	6·7

The results given in Table III. show how the potentials, required for striking and maintaining the arc with the furnace at 275° C., depend upon the current passing through the tungsten filament.

TABLE III.

Filament current.	Arc struck at	Arc maintained at
10·3 amp.	6·2 volts.	5·2 volts.
9·9	7·0	6·2
9·3	7·9	7·1
8·6	8·9	8·2
7·8	10·0	9·5
7·1	11·3	11·0

It was observed that the establishment of the arc at any applied voltage was always followed immediately by a fall in potential between the electrodes. This effect has also been noted in other experiments by the author *, and is similar to

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* Phil. Mag. xliv. p. 946 (1922).

that which characterizes the electric discharge through gases at low pressures.

In all these experiments it was noted that the arc, once struck, increased in brightness as the potential difference was raised, but with very dense vapours this increased brilliancy was very marked, and, in addition, a bright continuous spectrum was superimposed upon the arc line-spectrum. This continuous spectrum was entirely absent at low vapour-pressures.

It is evident from the results given above that the vapour density and the filament temperatures are two of the main factors involved in the production of low-voltage arcs in sodium vapour, the applied potential decreasing as the filament temperature and vapour density are increased. It is possible to strike the arcs at voltages well below the ionization potential—5·1 volts—demanded by the quantum theory, but this can be explained by "photo-impact" ionization, which is likely to be particularly prominent under the conditions existing when these low-voltage arcs are obtained.

4. *Experiments with Potassium Vapour.*

Some experiments were also made with potassium vapour, a tube similar to the one shown in fig. 1 being used. The arcing potentials depended upon the filament temperature in a manner similar to that experienced with sodium vapour, but they were not quite as uniform and concordant, and the arcs, once struck, were not as steady as with sodium vapour.

With the tungsten filament at white heat and the electric furnace at 420° C., the arc in potassium vapour was started easily between 3·5 and 4·0 volts. It would then persist with a lower applied potential. As the vapour-pressure was decreased the voltages required for striking and maintaining the arc were more nearly equal, the difference between these two values becoming greater at higher vapour densities. The decreased potentials necessary to start the arc as heavier currents were passed through the tungsten filament are shown in Table IV., the furnace being maintained at 420° C.

TABLE IV.

Filament current.	Arc struck at	Arc maintained at
8·9 amp.	3·9 volts.	2·8 volts.
8·6	4·2	3·1
8·2	4·4	3·5
7·7	4·8	4·2
7·2	5·7	5·4

The striking potentials decreased as the vapour density was raised both with tungsten and lime-coated platinum filaments, but, as with sodium vapour, the potentials were always a little smaller with tungsten than with the platinum. Table V. shows the effect of increasing the vapour density, the tungsten filament in each case being intensely bright.

TABLE V.

Temperature of furnace.	Arc struck at	Arc maintained at
214° C.	7·6 volts.	7·2 volts.
280°	6·0	5·5
322°	5·3	4·7
356°	4·7	3·9
404°	3·8	2·7

5. *Conclusions.*

The potentials necessary to strike and maintain arcs in sodium and potassium vapours depend primarily upon the vapour density and the temperature of the cathode, the potentials decreasing as the vapour density and the cathode temperature both increase. The voltage required to maintain such arcs is always less than that on striking, but the difference between these two values becomes smaller as the vapour density is lowered. Arcs, struck and maintained with potentials less than the ionization potential of the vapour, are obtained with intensely hot cathodes, the ionization in such cases arising, probably, from the absorption of radiation emitted from atoms already excited but not ionized. Such ionization by "photo-impact" results in complete ionization of the vapour atoms by electrons, none of which have a velocity greater than that corresponding to the resonance potential.

The spectra of such low-voltage arcs have been investigated, and the results obtained will be communicated in another paper.

The author wishes to express his sincere thanks for a Government grant, through the Royal Society, which enabled him to carry out these investigations.

CVI. *On the Dielectric Constants of some Liquids, and their Variation with Temperature.* (Part I.) *By* G. ERIC BELL, *B.Sc., and* FRANK Y. POYNTON, *B.Sc., Physics Research Laboratory, University College, Nottingham* [*].

Introduction.

INVESTIGATIONS on Dielectric Constant, and in particular its variation with temperature, have been the subject of several recent experimental researches. Theoretical work of Debye [†], Gans [‡] and others on the modification of the Clausius-Mosotti law have pointed to the possibility of obtaining from accurate measurements in this region considerable information with regard to the molecular structure of the dielectric.

Experimental Method.

The apparatus used consists essentially of two valve-maintained oscillatory circuits, which are in every case tuned so that the heterodyne note beats slowly with a third valve-maintained circuit oscillating at audible frequency.

If n_1 and n_2 are the frequencies of the two high-frequency oscillatory circuits, the frequency of the heterodyne-beat note is given by $n=n_1-n_2$, and if the frequency of the audible circuit is n', the beat-frequency observed in the telephones is given by $n-n'$.

The frequency of the valve-maintained circuits with the experimental condenser out is given, very approximately, by the relation

$$n=\frac{1}{2\pi\sqrt{L(C_0+C_1)}},$$

where C_0 is a constant depending on the distributed capacity of the circuit, C_1 is the capacity of the condenser, and L is the inductance in the circuit.

If the experimental condenser is put in the circuit, the frequency is given by

$$n=\frac{1}{2\pi\sqrt{L(C_0+C_1'+S)}}.$$

If C_1' is adjusted so that n remains constant, we have $S=C_1-C_1'$.

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[*] Communicated by Prof. E. H. Barton, D.Sc., F.R.S., F. Inst.P.

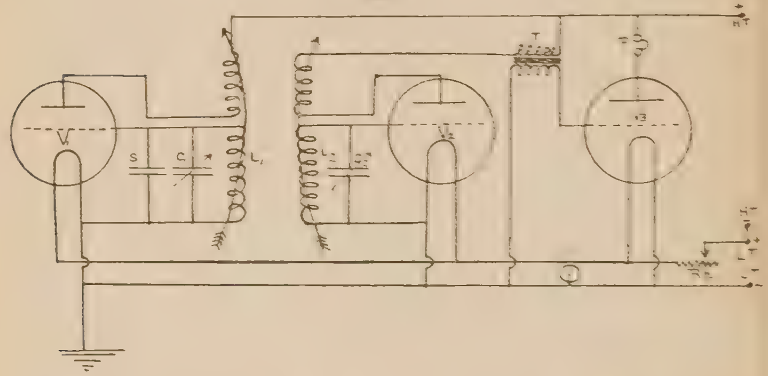
[†] P. Debye, *Physik. Zeitschr.* xiii. p. 97 (1917).

[‡] H. Isnardi u. R. Gans, *Physik. Zeitschr.* xxii. p. 230 (1921) & ix. p. 153 (1922).

Fig. 1 shows the arrangement diagrammatically. The coil L_1 together with the condensers C_1 and S in parallel constitute one oscillatory circuit maintained by the valve V_1. Similarly L_2 and C_2 form the second oscillatory circuit, maintained by the valve V_2. The transformer T and third valve V_3 form an amplifying unit, the advantage of which will appear later.

The audible frequency circuit is connected up exactly as the first oscillatory circuit, the condenser and coils being, of course, much larger.

Fig. 1.

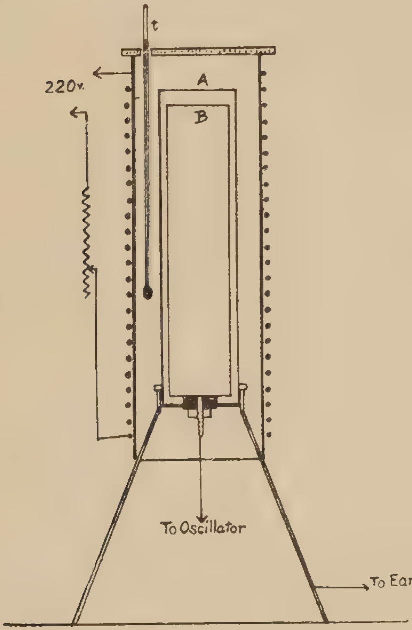


The coils used in the high-frequency circuits are duolateral coils wound on a two-inch former: by using coils having different numbers of turns, the frequency could be altered within certain limits, but over the small range which can be obtained in this way, the dielectric constant is practically independent of the frequency, so all the results have been obtained for one single frequency (of the order 4×10^5 cycles per second). C_1 is a Burndept "Low Loss" condenser, which is particularly suitable since it has good bearings and is efficiently screened from hand-capacity effects; C_2 is a Sullivan condenser, and S the "experimental condenser." The valves are Marconi-Osram R. 5v. and the transformer T by Pye's of Cambridge. The three circuits are all worked from the same H.T. battery, consisting of twenty-four large Leclanché cells, and also from the same L.T. battery, a 6-volt accumulator of very large capacity: a rheostat in the common L.T.+ lead serves to reduce the voltage across the valve-filaments to the correct five volts, as indicated by a voltmeter connected permanently across the L.T. leads.

Experimental Condenser.

Several forms of experimental condenser have been tried, designed for use in large boiling tubes; it is found, however, much more convenient to make the outer plate of the condenser at the same time the containing vessel. The form finally adopted is shown in section in fig. 2. A is a brass cylinder about 18 cm. long, closed at one end; B is a second brass cylinder 15 cm. long, closed at both ends and mounted coaxially with the first. The inner cylinder is mounted and insulated from the outer one as shown in detail in fig. 3. Mica is used as an insulating washer since the temperature variation of its dielectric constant is practically zero*.

Fig. 2.



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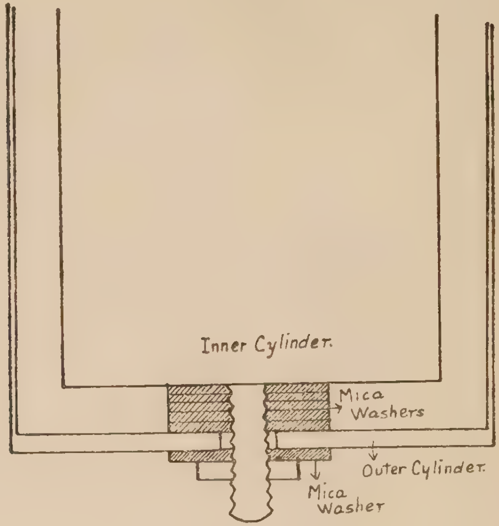
* See Dye and Hartshorn, Proc. Phys. Soc. xxxvii. (1924).

The capacity of the condenser, apart from the mica washer, is about 135 cm.

Fig. 3.



Heating Arrangements.

The lower end of the condenser fits into a ring supported on three legs. The temperature is controlled by means of a heating coil completely enclosing the condenser and supported on the same legs. A disk of asbestos board, with a hole to permit entrance of the thermometer, covers the top of the heating coil; this is found to ensure a more steady temperature being attained.

Details of Working.

Though the method is a simple one and capable of great accuracy, a number of precautions must be taken to ensure repeatable results. The whole apparatus with the exception of the experimental condenser and the batteries is contained in a large box, completely covered with tin-plate which is well earthed. The H.T. and L.T. batteries are contained in separate tin boxes also earthed. The leads from the experimental condenser, batteries, and phones are connected to suitable terminal boards at the back of the screened box. These earthed screens are necessary in order to eliminate external capacity effects and thus, in particular, to make the steadiness of the beat note independent of the movements of the observer. Apart, however, from such external screening, it is found very necessary to pay attention to several points in order to secure the requisite steadiness of the high-frequency oscillations. First, all contacts and condenser bearings etc. must be well made, and the whole apparatus protected from mechanical vibrations. Secondly, the L.T. accumulator must be of ample capacity, and even then steadiness cannot be obtained immediately after recharging. It would appear that the filament lighting is the main source of unsteadiness, and in this connexion we may note that there is considerable variation among the various types of valves, and after trials with a number we find Marconi Osram R. 5v. valves quite suitable for the purpose in hand. The low-frequency (audible) circuit keeps quite steady, as we have shown by comparison with tuning-forks. The amplifier permits the use of a loud-speaker which makes observation over long periods less tedious.

With regard to the arrangements for maintaining the experimental condenser at any given temperature, it is found that even after the thermometer has attained a steady state there is a slight drift of the beat note ; but since, after about an hour, this does reach a practically steady state, showing no variations capable of being measured on our compensating condenser, we feel confident that a state of thermal equilibrium persists in the heated enclosure, at the temperature given by the thermometer.

Results.

The results obtained for castor oil, olive oil, and linseed oil are given in the accompanying Tables and Curves. In each case a linear relation is found to hold between temperature and dielectric constant ; the dielectric constant at any temperature θ is related to that at 20° C. by the formula

$$K_\theta = K_{20}\,(1-(\theta-20)\,\alpha_{20}).$$

Values for α_{20} for the substance used are found to be :—

Caster Oil.	$\alpha_{20} = \cdot 0015.$
Olive Oil.	$\alpha_{20} = \cdot 0008.$
Linseed Oil.	$\alpha_{20} = \cdot 0009.$

TABLE I.

Castor Oil.	
Temp. °C.	Diel. Cons.
17·5	4·86
57·2	4·50
68·5	4·36
100	4·20
121·5	4·05
144	3·82
161	3·76
185	3·56
$\alpha = \cdot 0015$	

TABLE II.

Olive Oil.	
Temp. °C.	Diel. Cons.
18·5	3·21
62·5	3·12
75	3·06
92·5	3·01
121	2·94
146	2·87
172	2·79
$\alpha = \cdot 0008$	

TABLE III.

Linseed Oil.	
Temp. °C.	Diel. Cons.
19	3·24
62·5	3·15
88	3·04
114	2·96
136	2·95
158	2·82
174	2·81
$\alpha = \cdot 0009$	

Fig. 4.—Temperature Variation of Dielectric Constant of Castor Oil.

$\alpha_{20} = \cdot 0015$.

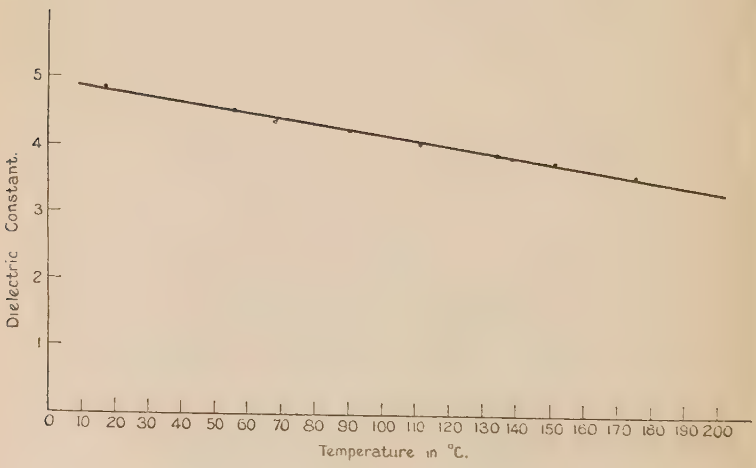


Fig. 5.—Temperature Variation of Dielectric Constant of Olive Oil.
$a_{20} = \cdot 0008$.

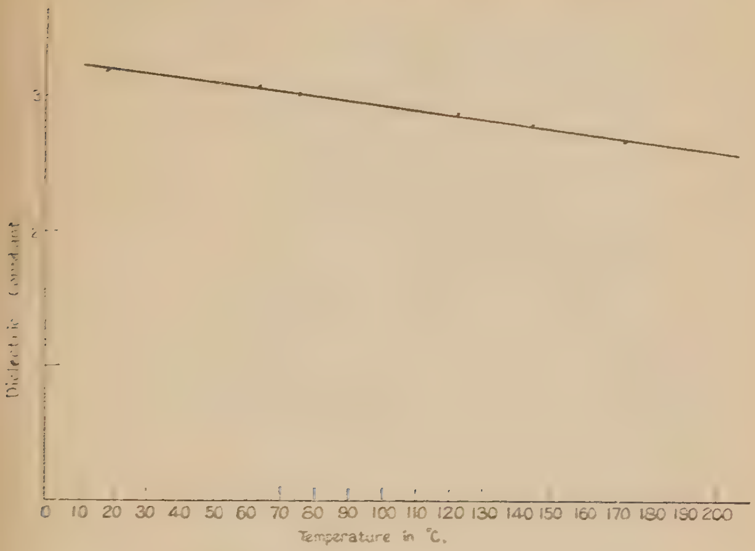
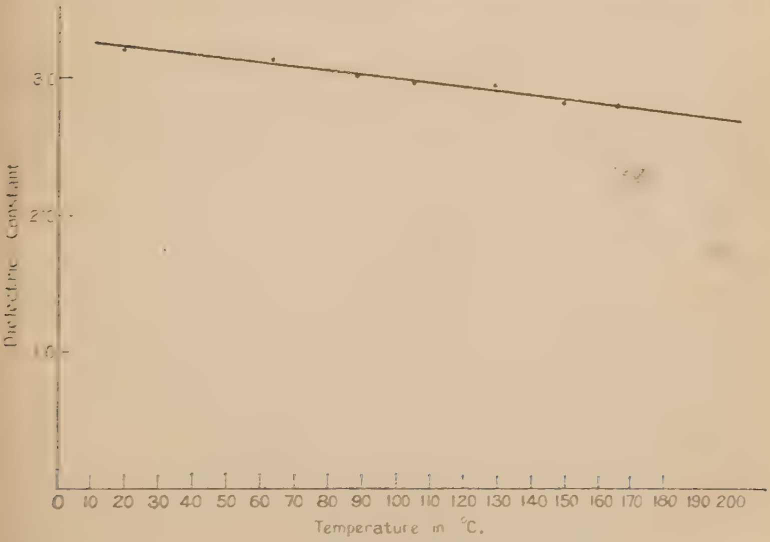


Fig. 6.—Temperature Variation of Dielectric Constant of Linseed Oil.
$a_{20} = \cdot 0009$.



Summary.

In this paper an account is given of the application of valve-maintained oscillatory circuits to the measurement of the dielectric constant of castor oil, olive oil, and linseed oil, with special reference to its variation with temperature. A linear relation is found to hold in each case.

Some of the difficulties of working with valve-maintained oscillatory circuits and the precautions taken to ensure steadiness are discussed in some detail.

This work is being extended to other liquids, and also over greater ranges of temperature.

In conclusion, the authors wish to express their thanks to Prof. E. H. Barton, D.Sc., F.R.S., for his interest and help, to Mr. A. H. Franks, B.Sc., for assistance in constructing parts of the apparatus, and to the Department of Scientific and Industrial Research for a grant by the aid of which the research has been carried out.

Physics Research Dept.,
University College, Nottingham
February 5, 1925.

CVII. *A Generalization of the Theory of Artificial Lines.* *By* The Research Staff of the General Electric Co., Ltd. (*Work conducted by* A. C. Bartlett.) *

An important class of electrical networks consists of artificial lines made up of numbers of symmetrical T or π sections, each section having 3 impedances elements of two different kinds. The theory of such lines can be expressed in terms of continued fractions of the form

$$a_1 + \frac{1}{a_2 +} \frac{1}{2a_1 +} \frac{1}{a_2 +} \frac{1}{2a_1 + \ldots\ldots}$$

A more general class, which so far has not received attention, can be constructed which consists of a series of similar symmetrical sections, each of which is composed of $2n-1$ elements of n kinds. A typical member of this class of section is shown in fig. 1 ; the centre element may be either shunt or series.

The theory of this more general class which involves the use of continued fractions such as

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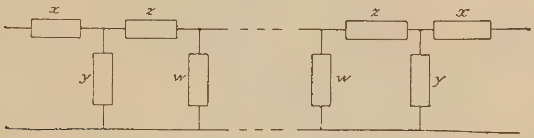
* Communicated by the Director.

$$a_1 + \frac{1}{\underset{*}{a_2}}\,\frac{1}{+\,a_3}+\ldots\frac{1}{a_{n-1}}+\frac{1}{a_n}+\frac{1}{a_{n-1}}+\ldots\frac{1}{a_3}+\frac{1}{a_2}+\frac{1}{\underset{*}{2a_1}}$$

can be readily developed by using certain theorems due to Muir relating fractions of this kind with Simple Continuants [†].

Fig. 1.



If the impedances of x, z, etc. (the series elements) are a_1, a_3, etc. and of y, w, etc. (the shunt elements) are $\frac{1}{a_2}$, $\frac{1}{a_4}$, etc., then the impedance of an artificial line consisting of an infinite number of such sections (*i. e.* the Line Characteristic Impedance Z_0) will be given by the recurring continued fraction

$$Z_0 = a_1 + \frac{1}{\underset{*}{a_2}}+\frac{1}{a_3}+\ldots\frac{1}{a_n}+\ldots\frac{1}{a_2}+\frac{1}{\underset{*}{2a_1}},$$

which is equal to (Muir, *l. c.*)

$$\sqrt{\frac{K(a_1, a_2, a_3 \ldots a_{n-1}, a_n, a_{n-1} \ldots a_3, a_2, a_1)}{K(a_2, a_3 \;\ldots\; a_{n-1}, a_n, a_{n-1} \;\ldots\; a_3, a_2)}}$$

$$= \sqrt{\frac{K(a_1, a_2 \ldots a_{n-1})\{K(a_1, a_2 \ldots a_{n-2}) + K(a_1, a_2 \ldots a_n)\}}{K(a_2, a_3 \ldots a_{n-1})\{K(a_2, a_3 \ldots a_{n-2}) + K(a_2, a_3 \ldots a_n)\}}}.$$

The propagation constant θ can be determined by considering the impedance $Z_0 \tanh \theta$ of a single section short-circuited at the far end.

Thus

$$Z_0 \tanh \theta = a_1 + \frac{1}{a_2}+\frac{1}{a_3}+\ldots+\frac{1}{a_n}+\ldots+\frac{1}{a_3}+\frac{1}{a_2}+\frac{1}{a_1}$$

$$= \frac{K(a_1, a_2 \ldots, a_n, \ldots a_2, a_1)}{K(a_2, a_3 \ldots, a_n, \ldots a_2, a_1)}$$

[†] 'Theory of Determinants,' 1882, chap. III.; also Proc. R. S. E. viii. pp. 229–236, and 'History of Determinants,' iii. p. 411 (1920).

of which the denominator is equal to

$$K(a_1, a_2 \dots a_n)K(a_2, a_3 \dots a_{n-1}) + K(a_1, a_2 \dots a_{n-1})K(a_2, a_3 \dots a_{n-2}).$$

Putting

$$\begin{aligned} K(a_1, a_2 \dots a_n) &= A_1, \\ K(a_1, a_2 \dots a_{n-1}) &= B_1, \\ K(a_1, a_2 \dots a_{n-2}) &= C_1, \\ K(a_2, a_3 \dots a_n) &= A_2, \\ K(a_2, a_3 \dots a_{n-1}) &= B_2, \\ K(a_2, a_3 \dots a_{n-2}) &= C_2, \end{aligned}$$

then

$$Z_0 = \sqrt{\frac{B_1(A_1 + C_1)}{B_2(A_2 + C_2)}},$$

$$\text{Tanh}\,\theta = \frac{\sqrt{B_1 B_2 (C_1 + A_1)(C_2 + A_2)}}{A_1 B_2 + B_1 C_2}.$$

But A_1, B_1, C_1, A_2, B_2, and C_2 are connected by the relations

$$\begin{aligned} A_1B_2 - A_2B_1 &= (-1)^n, \\ B_1C_2 - B_2C_1 &= (-1)^{n-1}, \\ A_1B_2 + B_1C_2 &= A_2B_1 + B_2C_1. \end{aligned}$$

Whence it follows that Z_0 and $\tanh\theta$ can be put in the form

$$\begin{aligned} Z_0 &= \frac{B_1}{B_2}\sqrt{\frac{X}{X-2}} \text{ if } n \text{ is even} \\ &= \frac{B_1}{B_2}\sqrt{\frac{X}{X+2}} \text{ if } n \text{ is odd ;} \end{aligned}$$

$$\begin{aligned} \text{Tanh}\,\theta &= \sqrt{1 - \frac{1}{(X-1)^2}} \text{ if } n \text{ is even} \\ &= \sqrt{1 - \frac{1}{(X+1)^2}} \text{ if } n \text{ is odd,} \end{aligned}$$

where $X = B_2(C_1 + A_1)$.

This form has the advantage that, if all the elements are reactances, the frequency ranges over which the artificial line has zero attenuation can be determined.

For the condition is that θ shall be purely imaginary, and this is seen to require that X be real, and lie between 0 and +2 if n is even, and between 0 and −2 if n is odd.

To illustrate the general theory, we may apply it to the artificial line composed of π sections; here $n=3$, while

a_1 is zero. If the impedances of the series and shunt elements are u and v respectively, then

$$a_1=0,$$

$$a_2=\frac{1}{v},$$

$$a_3=u,$$

$$A_1=K\left(0,\ \frac{1}{v},\ u\right)=u,$$

$$B_1=K\left(0,\ \frac{1}{v}\right)=1,$$

$$C_1=0,$$

$$B_2=K\left(\frac{1}{v}\right)=\frac{1}{v},$$

$$X=\frac{u}{v},$$

whence

$$Z_0=\frac{1}{\frac{1}{v}}\sqrt{\frac{\frac{u}{v}}{\frac{u}{v}+2}}=\frac{uv}{\sqrt{u^2+2uv}},$$

and

$$\tanh\theta=\sqrt{1-\frac{1}{\left(\frac{u}{v}+1\right)^2}}=\frac{\sqrt{u^2+2uv}}{u+v},$$

these being the well-known standard formulæ.

CVIII. *Ultimate Rational Units.*

By NORMAN CAMPBELL, *Sc.D.*

PROF. LEWIS is quite mistaken. I am so little dissatisfied with my formal argument that, while it remains unchallenged, it seems to me waste of time to discuss the doctrine which it proves to be false.

CIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlviii. p. 364.]

November 5th, 1924.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Prof. Franz Xaver Schaffer, of the State Natural History Museum, Vienna, delivered a lecture on The History of the Vienna Basin, of which the following is an abstract:—

After the withdrawal of the sea from Central Europe in Upper Oligocene time the transgression of the Lower Miocene (First Mediterranean Stage) took place along a narrow channel between the foot of the Alpine-Carpathian range and the old Bohemian massif, the sea reaching a height of more than 500 metres above the present sea-level. This narrow channel, which is called the 'Extra-Alpine Basin,' then underwent subsidence, resulting in a fall in the level of the sea, during which the so-called Schlier and the beds of Grund were deposited. The latter strata contain the richest subtropical molluscan fauna known in Central Europe. But the appearance of freshwater beds associated with the deposits of this shallow sea shows the interruption of former marine communications towards the west and north.

During the First Mediterranean Stage the region within the Alps, where the 'Intra-Alpine Basin' is now situated, began to subside along two faults running obliquely to the strike of the folds, in a north-and-south and north-east and south-west direction. In the triangular depression between them a freshwater lake was formed, with its level at first higher than that of the sea without, but was finally invaded by the marine waters carrying a rich fauna (Second Mediterranean Stage). The sea attained a height at this time of about 450 metres above the present sea-level, and the subsidence of the floor of this shallow bay continued. A connexion existed at first with the Mediterranean across the Hungarian basin, Serbia, and the Balkan Peninsula, but in later Miocene time a considerable part of this sea was cut off, and an inland sea stretched from Vienna as far as Turkestan. This was the Sarmatian Sea, the brackish waters of which contained a very stunted and uniform fauna, and reached about 400 metres above sea-level.

Then mountain-folding took place in the Transylvanian Alps, and the large inland sea was divided into an eastern 'Pontic' and a western 'Pannonian' basin. The water-level of the latter rose to about 450 metres, the freshwater conditions became more accentuated, and the fauna still more impoverished (Pontic Stage = Lower Pliocene).

More than 700 metres of sediments were deposited in the Intra-Alpine Basin after the Second Mediterranean Stage, during continued subsidence of its floor. Then, by an outflow through the

'Iron Gate' near Orsova, a gradual but intermittent sinking of the water-level took place, in accordance with a similar intermittent lowering of the base-level of erosion in the eastern region. Shore-lines have been eroded on the borders of the basin at about 230, 200, 150, 100, and 50 metres respectively above the present river-plain. The predecessor of the Danube had its inflow on the site of the city of Vienna, and deepened its channels in accordance with the levels of the lake, depositing gravels over the terraces lying at the above-mentioned altitudes. With the deposition of the 50-metre terrace the sedimentation under lacustrine conditions came to an end, and the river eroded the soft sediments and cut lower terraces into them during Quaternary time. Of these terraces only one, that at 15 metres, is preserved within reach of the city of Vienna.

December 3rd, 1924.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

The following communication was read :—

'A Composite Dyke from Eastern Iceland.' By Miss Eileen Mary Guppy, B.Sc., F.G.S., and Leonard Hawkes, M.Sc., F.G.S.

The composite dyke cuts the Tertiary plateau-basalts of Breiddal (Eastern Iceland) and in its fullest development comprises seven members, dolerites alternating with quartz-porphyries, the central rock being porphyry.

It is shown that the acid members resulted from one intrusive act, which took place after the intrusions giving rise to the dolerites. From the disposition of the chilled phases it is inferred that the acid magma came up before the middle of the last-formed basic dyke had completely cooled, and an attempt is made to estimate the time which elapsed between the intrusion of the basic and that of the acid magma.

The acid rock is crowded with dolerite-xenoliths. These have a regular distribution, and it is suggested that they originated through the shattering of basic dyke-rock in some other place by explosive action, with incorporation of the fragments in the magma before intrusion into its present position.

The felspar-phenocrysts of the acid rocks are soda-orthoclases with a small optic axial angle, and have a weathered appearance which is ascribed to incipient melting. They are compared with the artificially melted felspars described by A. L. Day & E. T. Allen. Some of the longer felspars are curved, this being considered a mechanical effect due to the flowage of the viscous acid magma.

Xenocrysts of quartz and soda-orthoclase are irregularly distributed through the dolerites. They are similar to the phenocrysts of the acid rocks, and occur in the same relative proportions. It is suggested that their presence in the dolerites is due to the admixture of a small amount of phenocryst-bearing acid magma.

Evidence is cited to show the great viscosity of the acid magma.

Possibly it directly overlay a basic magma, which was intruded first because of its greater mobility, and with which small quantities of the overlying acid liquor were drawn off. The final episode was the uprise of the acid residuum with explosive action.

In an Appendix Prof. H. Hilton calculates the probable rates of cooling of the middle and periphery of a dolerite-dyke.

December 17th, 1924.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Dr. John Downie Falconer, M.A., F.G.S., Director of the Geological Survey of Nigeria, delivered a lecture on the Geology of Nigeria, illustrated by maps and lantern-slides. The lecturer said that the geology of Nigeria has been known in outline for the last ten or fifteen years; but systematic study dates only from the establishment of the Geological Survey in 1919. The Pre-Cambrian rocks consist of quartzites, schists, amphibolites, banded and granitoid gneisses, and foliated and partly foliated granites, pierced by tourmaline-pegmatites which are themselves in places foliated and in places tin-bearing, with the tinstone as a primary constituent. The latest component of the crystalline group is a Younger Intrusive Series, entirely non-foliated and ranging in composition from gabbro to granite, with the latter predominating. There is no evidence for assigning to this series any other than a Pre-Cambrian age. The succession has been from basic to acid, with intrusive rhyolites and quartz-porphyries immediately preceding the granite.

The Younger Granite is rich in soda, and exhibits both a biotitic and a riebeckitic facies, the latter usually local and marginal. After consolidation the granite was broken and fissured, and subjected to pneumatolytic alteration and mineralization, with the formation of tinstone, topaz, wolframite, blende, and pyrites. The older rocks adjoining the granite were also extensively fractured and broken, and subjected to similar alteration and mineralization contemporaneously with the granite. The pneumatolysis is marked by the complete absence of tourmaline, while tinstone is associated most abundantly with the alteration of the biotitic facies of the granite.

Nigerian tinstone is thus of dual age and origin. It occurs with tourmaline as an original constituent of the older pegmatites, and with topaz in the pneumatolytic modifications of the younger granite and surrounding rocks. The granite is by far the richer source, and has shed the larger part of the tinstone which is now being recovered from the alluvial deposits of the tinfields.

The sedimentary rocks of Nigeria consist of Cretaceous and Tertiary strata, separated by an unconformity. The former have been investigated in the vicinity of the Government colliery, and have been subdivided into four groups: the Lower Shales of marine origin, the Upper Shales of estuarine origin, the Coal Measures, and the Sandstone Group. These groups are in conformable succession, and, despite the occurrence in the Upper Shales of certain plants with Tertiary affinities, they are believed to represent accumulations of Cretaceous age from Turonian upwards.

The Tertiary rocks have been studied along the Eastern Railway between the coalfield and the sea, and have been subdivided into a lower sandstone group, an estuarine group with a middle Eocene fauna (Bende-Ameki Beds), a lignite group, and a group of unconsolidated sands and clays (Benin Sands). There is a well-marked unconformity between the Cretaceous and the Tertiary, and it is believed that the various groups of Tertiary rocks are also separated by unconformities. Fossiliferous Tertiary deposits have been located in other parts of Nigeria; but the classification established for the Eastern Railway cannot yet be extended to the other Tertiary areas.

The volcanic rocks of Nigeria have been investigated to some extent on the central tinfields, where an older and a younger group have been distinguished. Both are basaltic in character, and the older was subjected to considerable erosion before the effusion of the younger. Ancient river-beds with tin-bearing gravels occur beneath both groups of volcanic rocks.

January 7th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

The following communication was read:—

'The Geology of the Rhobell Fawr District (Merionethshire).' By Alfred Kingsley Wells, M.Sc., F.G.S.

The area described covers some 30 square miles centred about the mountain-mass of Rhobell Fawr. The succession ranges from low down in the *Lingula* Flags to the Bala Mudstones.

The Cambrian rocks do not differ essentially from their equivalents in the Arthog—Dolgelley and Arenig—Moel Llyfnant districts, although the Tremadoc Beds are less completely developed, not extending far above the *Dictyonema* Band.

A feature of special interest is the development of an igneous cycle at a lower level than anywhere else in North Wales. The Rhobell Volcanic Group comprises an extrusive phase, the products of which were largely pyroclastic in origin and andesitic in composition; and a phase of minor intrusions when sills of hornblende-porphyrite and allied types were injected into the Upper Cambrian rocks in the neighbourhood of the volcanic centre, and dykes of similar composition penetrated the lower rocks of the Harlech Dome. The centre of eruption of which Rhobell is the denuded basal wreck, was a subaërial volcano which became active during the pre-Arenig interval. A further period of erosion was terminated by the transgression of the early Arenig sea, and the rocks of the Basement Group were deposited, these being derived from the denudation of a cone lying some distance east of Rhobell. The higher part of the Ordovician succession is condensed, the Lower Acid Volcanic Group of Cader Idris thins out in the south of the area, the zone of *D. bifidus* is feebly represented, and the *D.-murchisoni* Zone is probably absent. Fossils characteristic of the zone of *Glyptograptus teretiusculus* occur in mudstones at the base of the main volcanic series.

The Llandeilo Volcanic Group, the products of a submarine volcano, present many features of interest. Associated with thick felspar-crystal-tuffs are several flows of pillow-lava. The lowest is a normal basalt varying in texture from variolitic to doleritic, while the remainder are typical spilites. The andesitic magma of Arenig Mountain penetrated only into the extreme north of the area.

Unfossiliferous grey shales, the probable equivalents of the Llyn Cau Mudstones, were laid down during a period of normal sedimentation, during which the magma became more acid, so that the highest volcanic rocks, belonging to the Upper Acid Volcanic Group, include fragmental quartz-keratophyres. The active period of vulcanicity ceased finally and abruptly, the highest volcanic rocks being succeeded by a great thickness of Bala Mudstones.

Basic intrusions are common at several horizons between the Dolgelley Beds and the Upper Acid Group, and are without exception sills. The rocks range from gabbro through gabbroid dolerite, ophitic and subophitic dolerite, to porphyritic and spilitic types scarcely distinguishable from the basic lavas. They are believed to represent the phase of minor intrusions connected with the Llandeilo Volcanic Group. The area provides good illustrations of the action of an intrusive magma in persistently flooding certain horizons and invading selected rocks while leaving others unaffected.

As a consequence of its position at the south-eastern 'corner' of the Harlech Dome, the strike changes almost through a right-angle in passing from south to north. Folding along north-and-south axes is dominant, but the folds have been buckled against the Rhobell mass which acted as a resistant knot lying in advance of the hard core of the Dome. The area is much faulted, the most important dislocations being parallel to those recently described from the Bala district.

Complete chemical analyses of the chief rock-types have been made by Dr. H. F. Harwood.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]